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PRELIMINARY NUMERICAL ANALYSIS OF  
IMPROVED GAS CHROMATOGRAPH MODEL

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Mars Exploration

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## ABSTRACT

In continuance of system studies on the science package for an unmanned Martian roving vehicle, a new mathematical model for the gas chromatograph has been developed which incorporates the heretofore neglected transport mechanisms of intraparticle diffusion and rates of adsorption. Moment analysis of this Inter-Intraparticle Adsorption Model has showed the model to be more capable of predicting spreading in experimental chromatograms. Because a closed-form analytical solution to the model does not appear realizable, techniques for the numerical solution of the model equations are being investigated. Criteria have been developed for using a finite terminal boundary condition required in numerical solutions in place of an infinite boundary condition used in analytical solution techniques. The method of Finite Differences appears computationally inefficient for application to equations of the type to be solved. The class of Weighted Residual methods known as Orthogonal Collocation is presently being investigated and appears promising.

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I. INTRODUCTION AND SUMMARY

The mathematical modelling of the gas chromatograph is one sub-task of a group effort designed to define fundamental system design criteria necessary for an optimal design of a combination gas chromatograph - mass spectrometer which is to be part of an unmanned mission to Mars. The task which must be performed by this part of a Martian Roving Vehicle is the analysis of samples to determine the existence of organic matter and living organisms on the Martian surface. The analysis will involve the subjection of gaseous, liquid, and solid samples to biological and chemical reactions, with subsequent product separation and identification using the gas chromatograph - mass spectrometer system.

The chromatograph may be looked upon as a separating device where the phenomenon of adsorption-desorption is utilized. Owing to the different characteristics of various chemicals, each species will adsorb and desorb at different rates when exposed to a packed bed of granular particles with or without a liquid substrate. Because of the unique behavior of each chemical, a multi-component sample may be injected into a chromatograph and elute as separate waves of specific chemical species.

The transport mechanisms which have been included in previous model formulations are all interparticle mechanisms with simple adsorbed phase behavior assumed. These previous model formulations have proven incapable of adequately predicting component behavior in all cases. Consequently, a new model is developed which includes both interparticle



and intraparticle transport mechanisms. This model is analysed in the Laplace transform domain using the method of moments. The first three moments of the impulse response of the model are derived. Using actual input data, predictions for the first three moments of the output data are made and are compared with actual output data and predictions of a simpler interparticle model. The results indicate that the new model is more capable of the prediction of the moments of the actual data.

Because the mathematical complexity of the new model prohibits a direct, closed-form analytic expression for a response, investigation of numerical techniques applicable to the equations of the old and new models is made. The numerical techniques require a finite terminal boundary condition as opposed to an infinite column boundary condition used in analytic solution (when possible) of the chromatographic model partial differential equations. Using a simple, transient diffusion-convection equation, criteria are developed wherein a finite terminal boundary condition can be applied to yield infinite column behavior at the bed outlet.

An analysis of two methods for the numerical solution of partial differential equations of the type encountered in the chromatograph modelling work is subsequently made. The technique of Finite Differences is rejected due to excessive computer time required to produce model simulations. The technique of Orthogonal Collocation, while not established as the best method, offers promise and is the current area of modelling endeavor.

## II. CHROMATOGRAPH SYSTEM MODELLING

### A. Chromatograph Modelling Background

One area of the overall gas chromatograph systems study has been the mathematical modelling of the chromatograph system. Work in this area has been carried out by several investigators (Sliva, 1968; Voytus, 1969; Taylor, 1970; Keba and Woodrow, 1972). A course has been pursued wherein successively more complex models have been considered. These models have all yielded analytical expressions from which a simulated chromatogram could be computed directly. Comparison of predicted system behavior with actual system data has directed modelling efforts to consider more adequate and hence more complicated models.

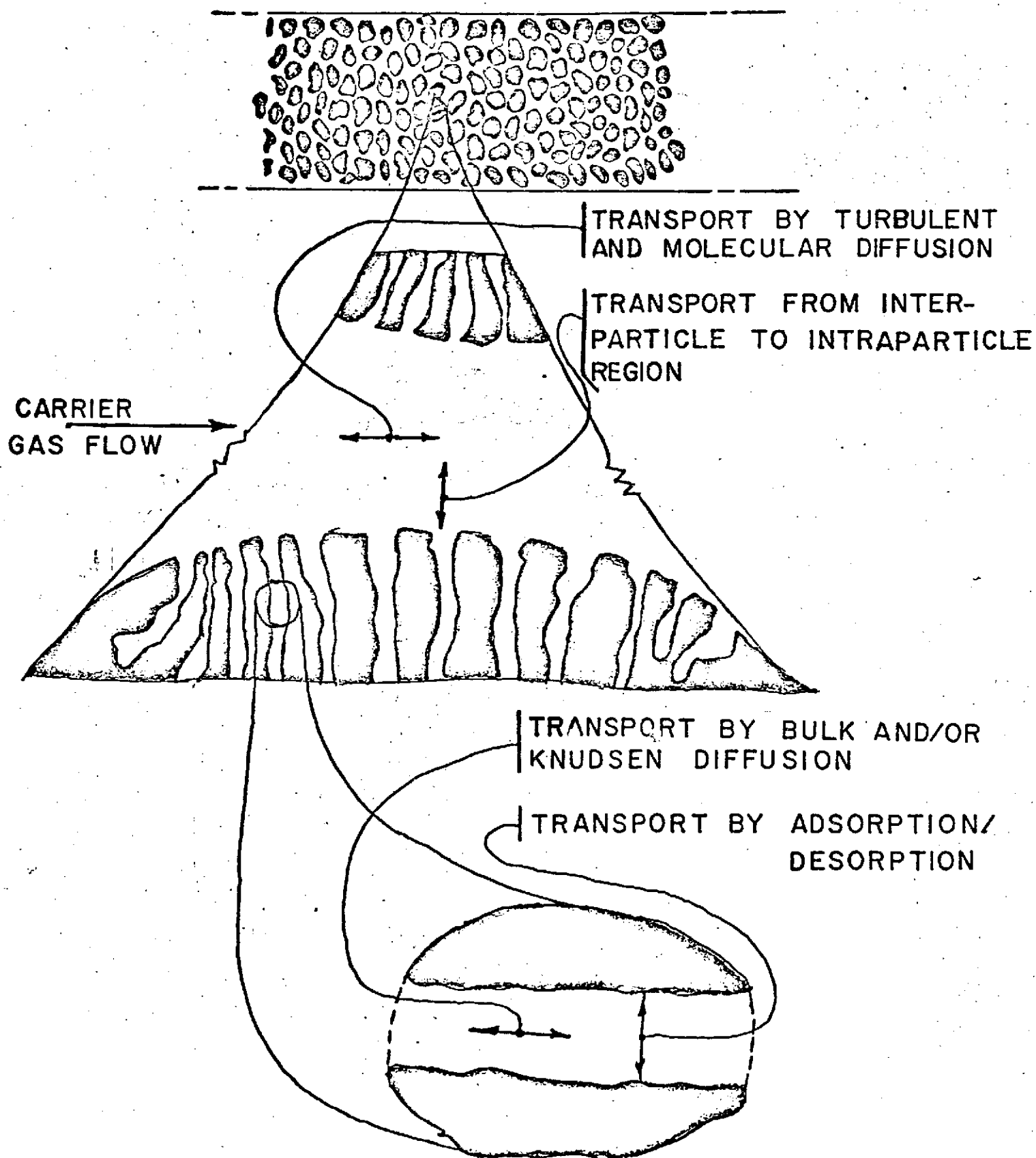
Prior to this investigation, the most complex model proposed for the chromatograph system was based on an interparticle phase mass balance and an adsorbed phase mass balance. Several transport mechanisms were included: axial diffusion, convection, and mass transfer between the interparticle and adsorbed phases. A linear isotherm was used to describe the adsorption kinetics. This model has been studied and compared (Keba and Woodrow, 1972) for the cases of finite rates of mass transfer to the adsorbed phase (nonequilibrium adsorption) and infinitely high rates of mass transfer to the adsorbed phase (equilibrium adsorption). In both cases, simulations using the models failed to predict the degree of dispersion exhibited by many of the experimental data. It was concluded that additional transport mechanisms, e.g., intraparticle diffusion, may be contributing appreciably to the overall adsorption-desorption process. Hence, further model development and analysis was indicated.

### B. Development of the Inter-Intraparticle Adsorption Model

Previously, the intraparticle region of the chromatograph packing material has been modelled as being nonexistent or as a region where the transport processes occur at such a rapid rate so as not to significantly affect the dynamic behavior of the system. It is the purpose of this section to reformulate the chromatograph system model by including the transport processes which are presumed most likely to affect the dynamics of the adsorption-desorption process within the chromatograph packing material.

Figure 1 presents graphically the transport processes to be modelled. The sample to be separated is injected into a relatively inert carrier gas, e.g., helium. As this slug of sample is transported down the chromatograph by the carrier gas, the various species diffuse, adsorb, and desorb. Diffusion of the chemicals in the direction of the carrier gas flow in the interparticle region is represented by the dimensionless parameter,  $Pe_E$ , which is determined by the system fluid mechanics. Mass transport from the interparticle region to the intraparticle region is represented by a dimensionless parameter,  $N_{toG}$ , which is essentially determined by the system fluid mechanics. Diffusion in the intraparticle region is represented by dimensionless parameter,  $Pe_A$ , which is in part determined by the properties of the particle packing. The rate of adsorption within the particle is characterized by the dimensionless parameter,  $N_{RU}$ . Adsorption-desorption within the particle is represented by  $mR_T$ , a thermodynamic parameter peculiar to each species. This parameter contains an equilibrium constant,  $m$ ,

# CHROMATOGRAPHIC COLUMN INTER-INTRAPARTICLE MODEL CONCEPTS



and the quantity  $R_I$ .  $R_I$  is the ratio of moles of fluid within the particle to the moles of adsorptive sites within the particle. The quantity  $R_I$  is directly related to the quantity  $R_0$  where  $R_0$  is the ratio of moles of fluid within the total bed to the moles of adsorptive sites within the total bed. The relationship between these quantities is

$$R_I = \left[ \left( \frac{\epsilon}{1-\epsilon} \right) / \beta \right] R_0 \quad (1)^*$$

The reason for noting this relationship so that the parameter  $mR_0$  has been noted in previous models and the above relationship serves as a unifying concept for the new model formulation which follows.

With the above concepts in mind, the following set of dimensionless equations has been derived\*\* based on the assumptions which follow:

An interparticle phase mass balance:

$$\left( \frac{1}{Pe_E} \right) \frac{\partial^2 y}{\partial z^2} - \frac{\partial y}{\partial z} - N_{toG} (y - y_i)_{r=1} = \frac{\partial y}{\partial \theta} \quad (2)$$

An intraparticle phase mass balance:

$$\left( \frac{1}{Pe_A} \right) \left( \frac{L}{R} \right)^2 \left[ \frac{\partial^2 y_i}{\partial r^2} + \frac{2}{r} \frac{\partial y_i}{\partial r} \right] - N_{RU} (y_i - y_i^*) = \frac{\partial y_i}{\partial \theta} \quad (3)$$

---

\* See Section IX, Nomenclature, for definition of terms.

\*\* See Appendix A for derivation.

An adsorbed phase mass balance:

$$\left(\frac{1}{R_I}\right) \frac{\partial x_a}{\partial \theta} = N_{RU} (y_i - y_i^*) \quad (4)$$

A thermodynamic relationship between the intraparticle and adsorbed phases:

$$y_i^* = m x_a \quad (5)$$

The above equations are valid under the following assumptions:

1. The column is isothermal.
2. The carrier gas velocity profile is flat.
3. The axial diffusion coefficient is a composite factor which may or may not have a turbulent component.
4. The gas composition is approximately constant in the radial direction at a given axial position. The concentration gradient occurs in a thin boundary layer at the interparticle-intraparticle interface.
5. The gas composition within the particle is approximately constant in the angular direction at a given radial position; the concentration gradient occurs only in a thin boundary layer near the adsorbent surface.
6. The adsorbent layer is so thin that there is no diffusional resistance within the layer in the direction normal to the surface.
7. The diffusivity in the adsorbent layer is so small that there is no diffusion in the direction parallel to the

surface in the intraparticle radial direction.

8. The net rate of adsorption for the carrier gas is negligible.
9. Only one component is adsorbed and its gas phase composition as a mole fraction is small compared to unity.
10. The carrier gas behaves as an ideal gas.

An applicable set of boundary and initial conditions are as follows:

Initial Conditions:

$$y(z, 0) = 0 \quad (6)$$

$$y_i(z, r, 0) = 0 \quad (7)$$

$$x_a(z, r, 0) = 0 \quad (8)$$

Boundary Conditions:

$$y(0, \theta) = A_\theta \quad (9)$$

$$\left[ \left( \frac{\beta}{\epsilon} \right) a L \left( \frac{L}{R} \right) / Pe_A \right] \frac{\partial y_i}{\partial r} = N_{toG}(y - y_i); \text{ when } r=1 \dots \quad (10)$$

$$\frac{\partial y_i}{\partial r} = 0 \quad ; \quad r = 0 \quad (11)$$

$$\lim_{z \rightarrow \infty} y(z, \theta) = \text{finite} \quad (12)$$

These conditions reflect a sample-free column at zero time, a sample injected as an impulse, mass transfer between the interparticle and intraparticle regions, no concentration gradient at the center of the

column packing, and no end effects at the column exit.

For the systems under consideration it has been shown by Keba and Woodrow (1972) that inclusion of the parameter  $N_{toG}$  is of minor importance. If one were to consider the case of infinite rates of mass transfer, i.e.,  $N_{toG} \rightarrow \infty$ , the coupling condition given by equation (10) would be replaced by

$$y_i(z, l, \theta) = y(z, \theta) \quad (13)$$

Thus, a model in the form of a set of coupled, partial differential equations is proposed. Prior to consideration of the time domain solution of the equations, a moment analysis can be made to ascertain the predictive capabilities of the proposed model. This analysis is the subject of the next part of this report.

### III. MOMENT ANALYSIS OF THE INTER-INTRAPARTICLE ADSORPTION MODEL

#### A. Theory and Background

An analysis of a proposed model can be made prior to determination of the model's time-domain solution to yield the gross characteristics of the impulse response of the model. In addition, because of the poor predictions of previous models with respect to chromatogram spreading, it is desirable to know the nature of the response of the proposed model for the pulse-type forcing functions used in experimental work. The nature of the response can be characterized by statistical quantities known as moments which may be obtained without knowledge of the time-domain model solution. The moments may be derived directly from the Laplace domain solution of the model. The following develop-



ment will indicate how the moments of a model are obtained and how the analysis can be extended to give the moments of systems forced by general pulse-type inputs.

The impulse response of the chromatograph may be viewed as the residence time frequency distribution (Douglas, 1972). This quantity resembles the probability distribution function which appears in statistical analysis. The moments of the distribution function about the time origin are defined by the following:

$$\mu_n = \int_0^{\infty} \theta^n f(\theta) d\theta / \int_0^{\infty} f(\theta) d\theta \quad (14)$$

where

$f(\theta) \triangleq$  the distribution function being analysed.

The denominator of equation (14) is the area under the function. The relationship of the moments about the origin to the Laplace transform is developed in Appendix B. The result is:

$$\mu_n = (-1)^n \lim_{s \rightarrow 0} \left\{ \frac{\partial^n}{\partial s^n} [\tilde{f}(s)] \right\} / \lim_{s \rightarrow 0} \tilde{f}(s) \quad (15)$$

where

$$\tilde{f}(s) = L[f(\theta)] \triangleq \int_0^{\infty} e^{-s\theta} f(\theta) d\theta \quad (16)$$

Interest also centers on the moments about the first absolute moment or mean,  $\mu_1$ . Mathematically these moments are defined by:

$$\bar{\mu}_n = \int_0^{\infty} (\theta - \mu_1)^n f(\theta) d\theta / \int_0^{\infty} f(\theta) d\theta ; n \geq 2 \quad (17)$$

These moments about the mean  $\mu_1$ , are directly related to the moments about the origin. The relationships are obtained by formal expansion of equation (17). Appendix B gives the relationships for  $n=2$  and  $n=3$ . For  $n=2$ , the moment about the mean is exactly the variance of the response. For  $n=3$ , the moment about the mean is related to the skew of the response.

One can use the preceding to develop equations relating the moments of system responses for arbitrary pulse-type forcing functions (see Appendix B for details). That is, given the system input data (the moments of which can be computed from equation (14)) and the system transfer function (the Laplace transform of the impulse response), the moments of the system response may be determined and compared with the moments of the actual output data. Referring to the block diagram in Figure 2, the results are:

$$A_Y = A_X \cdot A_G \quad (18)$$

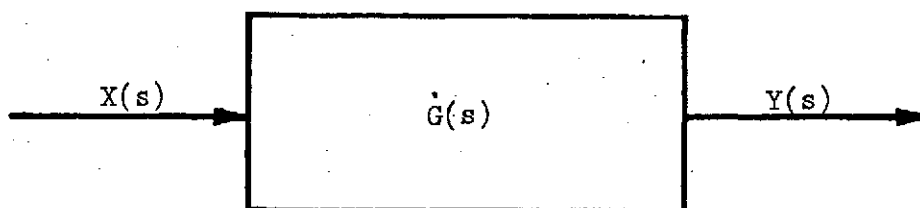
$$\mu_{1Y} = \mu_{1X} + \mu_{1G} \quad (19)$$

$$\bar{\mu}_{2Y} = \bar{\mu}_{2X} + \bar{\mu}_{2G} \quad (20)$$

$$\bar{\mu}_{3Y} = \bar{\mu}_{3X} + \bar{\mu}_{3G} \quad (21)$$

Equation (18) states that the area under the output curve is the product of the area under the input curve and the impulse response curve.

Equation (19) states that the mean of the output occurs at the sum of the mean of the input function and impulse response. Equation (20) states that the variance of the output is the sum of the variance of the input function and the variance of the impulse response. Equation



$X(s) = \mathcal{L} [x(\theta)]$  ;  $x(\theta)$  is the forcing function

$Y(s) = \mathcal{L} [y(\theta)]$  ;  $y(\theta)$  is the system response

$G(s)$  = system transfer function

Figure 2. Typical System Block Diagram

(21) states that the third moment about the mean of the output is the sum of the third moments about the means of the input function and impulse response, respectively.

This technique can also be used for estimating system parameters. Douglas (1972) uses an equation similar to equation (20) to estimate an axial Peclet number for a packed bed. Schneider and Smith (1968) apply moment analysis to estimate adsorption equilibrium constants, rate constants, and intraparticle diffusivities for a chromatographic system modelled similarly to that of Part II. However, accurate parameter estimation using this method is limited by the accuracy of the data used for analysis.

#### B. Application of Moment Analysis to the Inter-Intraparticle Adsorption Model

The previous section outlined a method which can be used to analyse pulsed systems to determine the gross characteristics of the system response. This section will document an application of the concepts of moment analysis to the proposed model of Part II.

Consider the set of partial differential equations, boundary conditions, and initial conditions, equations (2) through (12). A Laplace transform domain solution for the impulse response or transfer function was derived and appears in Figure 3; details appear in Appendix C.

Applying the definition given by equation (15) and using equation (17), the moments  $\mu_1$ ,  $\bar{\mu}_2$ , and  $\bar{\mu}_3$  are derived for the impulse response of the Inter-Intraparticle Adsorption Model. The

$$Y(1,s) = \exp \left\{ \frac{Pe_E}{2} - \sqrt{\frac{Pe_E^2}{4} + \gamma(s) Pe_E} \right\}$$

where:

$$\gamma(s) = N_{toG} (1 - \lambda(s)) + s$$

$$\lambda(s) = \frac{b \sinh(\sqrt{a_1})}{[(b-1)\sinh(\sqrt{a_1}) + \sqrt{a_1} \cosh(\sqrt{a_1})]}$$

$$a_1(s) = \left\{ \left[ \frac{-N_{RU}^2 mR_I}{(s + N_{RU} mR_I)} + N_{RU} + s \right] \left( \frac{R}{L} \right)^2 Pe_A \right\}$$

$$b = \frac{N_{toG}}{3 \frac{\beta(1-\epsilon)}{\epsilon} \left( \frac{L}{R} \right)^2 \frac{1}{Pe_A}}$$

$$\beta = \text{Particle porosity}$$

$$\epsilon = \text{Bed void fraction}$$

Figure 3. Transfer Function for the Inter-Intraparticle Adsorption Model.

results are presented in Figure 4; details of the manipulations appear in Appendix D.

The parameters  $Pe_E$ ,  $N_{toG}$ , and  $Pe_A$  can be estimated a priori. The parameters  $mR_O$  and  $N_{RU}$  are not predictable a priori. Previous modeling analysis has estimated  $mR_O$  by a curve fitting process (Benoit, 1971). The estimation of  $N_{RU}$  will most likely involve curve fitting also.

An analysis was made using existing single component data. The parameters  $Pe_E$ ,  $Pe_A$ , and  $N_{toG}$  were estimated using existing correlations. The values of  $mR_O$  which were estimated by Keba and Woodrow (1972) using simpler models were used and the parameter  $N_{RU}$  was varied. Tables 1 and 2 give results of this analysis for acetone at 100° C and ethylene at 50° C. Both experiments used Chromasorb 102 column packing a porous material. In each case, the moments for the impulse response of the model were computed using the equations given in Figure 4. Use of system input data and equations (19) through (21) give predictions as a function of  $N_{RU}$  for the output moments. These predicted values are compared with actual moments of the output data and with the predictions of the simpler, interparticle equilibrium adsorption model. Expressions for the moments of the simpler model were initially developed by Voytus (1969).

The results indicate that the proposed model can more closely predict the characteristics of the output data than the simpler, interparticle model. The results indicate that a value of  $N_{RU}$  on the order of several hundred will give a predicted second moment very

$$\mu_1 = 1 + 1/mR_0 + (1-\epsilon) \beta/\epsilon$$

$$\bar{\mu}_2 = 2 (\mu_1)^2 / Pe_E + 2 [(1-\epsilon) \beta/\epsilon] \left\{ (1 + 1/mR_I)^2 \left[ (R/L)^2 Pe_A/15 + (1-\epsilon) \beta/\epsilon N_{toG} \right] + 1/N_{RU} (mR_I)^2 \right\}$$

$$\begin{aligned} \bar{\mu}_3 = 6 \mu_1 \bar{\mu}_2 / Pe_E + 6 [(1-\epsilon) \beta/\epsilon] \left\{ 2 [(1 + 1/mR_I)/N_{RU} (mR_I)^2] \left[ (R/L)^2 Pe_A/15 \right. \right. \\ \left. \left. + (1-\epsilon) \beta/\epsilon N_{toG} \right] + (1 + 1/mR_I)^3 [(1-\epsilon) \beta/\epsilon N_{toG}]^2 \right. \\ \left. + 2 (1-\epsilon) \beta (R/L)^2 Pe_A/15 \epsilon N_{toG} - 23 (R/L)^4 Pe_A^2 / 315 \right] \\ \left. + 1/N_{RU}^2 (mR_I)^3 \right\} \end{aligned}$$

Figure 4. Moments of the Impulse Response of the Inter-Intraparticle Adsorption Model.

TABLE 1

## MOMENT ANALYSIS AND PARAMETRIC

STUDY - ACETONE 100°C.

$mR_0$	$\mu_{1, \text{observed}}$	(1) $\mu_{1, \text{predicted}}$	(2) $\mu_{1, \text{predicted}}$
0.029	173.29	158.69	156.49
$N_{RU}$	$\mu_{2, \text{observed}}$	(1) $\mu_{2, \text{predicted}}$	(2) $\mu_{2, \text{predicted}}$
100	815.67	977.55	437.28
200		723.41	
400		686.34	
800		517.80	
1600		483.53	
3200		466.40	
6400		457.83	
12800		453.55	
25600		451.41	
$N_{RU}$	$\mu_{3, \text{observed}}$	(1) $\mu_{3, \text{predicted}}$	(2) $\mu_{3, \text{predicted}}$
100	25404.0	23192.2	19499.2
200		20454.8	
400		19745.3	
800		19555.1	
1600		19501.7	
3200		19485.1	
6400		19480.4	
12800		19477.2	
25600		19476.2	

$$Pe_E = 8689$$

$$N_{tOG} = 88960$$

$$(L/R)^2 / Pe_A = 328.2$$

- (1) Inter-Intraparticle Adsorption Model  
 (2) Interparticle Equilibrium Adsorption Model



TABLE 2

## MOMENT ANALYSIS AND PARAMETRIC

STUDY - ETHYLENE 50°C.

$mR_0$	$\mu_{1, \text{observed}}$	$\mu_{1, \text{predicted}}^{(1)}$	$\mu_{1, \text{predicted}}^{(2)}$
0.194	26.475	25.986	23.719
$N_{RU}$	$\mu_{2, \text{observed}}$	$\mu_{2, \text{predicted}}^{(1)}$	$\mu_{2, \text{predicted}}^{(2)}$
100	7.024	13.283	0.388
200		6.973	
400		3.817	
800		2.240	
1600		1.451	
3200		1.056	
6400		0.859	
12800		0.760	
25600		0.711	
$N_{RU}$	$\mu_{3, \text{observed}}$	$\mu_{3, \text{predicted}}^{(1)}$	$\mu_{3, \text{predicted}}^{(2)}$
100	19.623	13.049	0.191
200		3.519	
400		1.058	
800		0.403	
1600		0.219	
3200		0.163	
6400		0.144	
12800		0.137	
25600		0.134	

$$Pe_E = 9744$$

$$N_{tOG} = 79750$$

$$(L/R)^2 / Pe_A = 436.2$$

- (1) Inter-Intraparticle Adsorption Model  
 (2) Interparticle Equilibrium Adsorption Model

close to the second moment of the output data. This magnitude of  $N_{RU}$  is consistent with the values of  $N_{RU}$  which were obtained in independent research by Schneider and Smith (1968). Tables 1 and 2 further indicate that matching of the third moments would give different values of  $N_{RU}$ . However, the use of third moments is not as reliable because data inaccuracies are further magnified in the analysis.

It should be noted that if one accepts the value of  $N_{RU}$  as being on the order of several hundred for each case, all other parameters, excluding  $mR_0$ , are of the same magnitude. The key to the difference in the two component behaviors is the parameter  $mR_0$ .

#### IV. TERMINAL BOUNDARY CONDITION ANALYSIS

Mathematical modelling of chromatographic systems commonly require solutions to equations of the form:

$$(1/Pe) (\partial^2 y / \partial z^2) - \partial y / \partial z - R_A = \partial y / \partial \theta \quad (22)$$

Application of analytical techniques to the above equation, when possible, commonly utilize the terminal boundary condition

$$\lim_{z \rightarrow \infty} y(z, \theta) = \text{finite} \quad ; \quad \theta > 0 \quad (23)$$

Use of the above boundary condition in analytical work yields a great deal of mathematical simplification. In addition, the use of this boundary condition is consistent with the theory which has been developed for prediction of the dispersion in packed beds; see, for example, Gunn (1969).

However, when numerical techniques must be applied to solve equation (22), the terminal boundary condition given by equation (23) must be replaced by a terminal boundary condition which is both computationally expedient and physically meaningful. A finite terminal boundary condition which has found general usage in chemical reaction engineering problems (Wehner and Wilhelm, 1956) is:

$$\partial y(1, \theta) / \partial z = 0 \quad ; \quad \theta > 0 \quad (24)$$

Bastian and Lapidus (1956) considered the case where  $R_A$  in equation (22) was an adsorption term. A linear relationship was assumed to describe the adsorption kinetics. For a step-input and the conditions chosen, Bastian and Lapidus showed that finite column calculations, using equation (24) as a terminal boundary condition, closely approximated infinite column calculations, using equation (23) as a terminal boundary condition.

The analysis of chromatograph systems for pulse-type forcing functions has prompted consideration of the two terminal boundary conditions. The question arises as to how the use of a finite terminal boundary condition affects output prediction as compared to the infinite column case when the system is forced by pulse-type functions. It is desirable for the two predictions of column outlet behavior ( $z=1$ ) to be similar so that the use of a priori estimates of  $Pe$  are valid in complicated models having the form of equation (22).

In order to answer the above question and to establish the conditions under which a finite terminal boundary condition can be used

to yield infinite column behavior at the column outlet ( $z=1$ ), two relatively simple problems can be considered:

Case I:

$$(1/Pe) (\partial^2 y / \partial z^2) - \partial y / \partial z - R_A = 0 \quad (25)$$

$$y(z, 0) = 0 \quad ; \quad z > 0 \quad (26)$$

$$y(0, \theta) = \delta(\theta) \quad ; \quad \theta \geq 0 \quad (27)$$

$$\lim_{z \rightarrow \infty} y(z, \theta) = \text{finite} \quad (28)$$

$$R_A = 0 \quad (29)$$

and

Case II:

$$(1/Pe) (\partial^2 y / \partial z^2) - (\partial y / \partial z) - R_A = 0 \quad (30)$$

$$y(z, 0) = 0 \quad ; \quad z > 0 \quad (31)$$

$$y(0, \theta) = \delta(\theta) \quad ; \quad \theta \geq 0 \quad (32)$$

$$\partial y(z_0, \theta) / \partial z = 0 \quad ; \quad \theta > 0, \quad z_0 \geq 1 \quad (33)$$

and arbitrary

$$R_A = 0 \quad (34)$$

Case I considers the unit impulse response of the simple, one-dimensional, axial dispersion-convection model in an infinite column.

Case II considers the unit impulse response of the simple, one-dimensional, axial dispersion-convection model with the finite column boundary condition. It is desirable to determine the conditions under which the two

responses are equivalent. These conditions can be determined without resorting to the comparisons of the analytical solutions for each case, through use of the method of moments.

At a dimensionless length of unity, the column outlet, the Laplace transforms of the two solutions are\* :

Case I:

$$y(1, s) = \exp \left[ \left( \frac{Pe}{2} \right) - (\arg) \right] \quad (35)$$

Case II:

$$y(1, s) = \exp \left( \frac{Pe}{2} \right) \left\{ \left( \frac{Pe}{2} + \arg \right) \exp \left[ -(1-z_0) \cdot \arg \right] - \left( \frac{Pe}{2} - \arg \right) \cdot \exp \left[ (1-z_0) \cdot \arg \right] \right\} \left\{ \left( \frac{Pe}{2} + \arg \right) \exp \left[ z_0 (\arg) \right] - \left( \frac{Pe}{2} - \arg \right) \exp \left[ -z_0 (\arg) \right] \right\} \dots \quad (36)$$

where

$$\arg = \sqrt{Pe^2/4 + Pe s} \quad (37)$$

Each, respective output curve can be characterized by its moments. Two moments are considered here - the first moment about the origin and the second moment about the mean. The first moment about the origin gives the time of appearance of the mean of the output curve. The second moment about the mean gives the variance of the output curve. These moments, as has been previously noted in Part III, are directly obtainable from the Laplace transform domain solution. The general relationships were given in equations (14) through (17). Using these

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\* see Appendix E for details.

relationships, the Case I and Case II transfer functions were analysed to yield:

$$\mu_{1_I} = 1 \quad (38)$$

$$\bar{\mu}_{2_I} = 2 / Pe \quad (39)$$

and

$$\mu_{1_{II}} = 1 + \left[ \exp(-Pe Z_0) - \exp(Pe - Pe \cdot Z_0) \right] / Pe \quad (40)$$

$$\begin{aligned} \bar{\mu}_{2_{II}} = & 2/Pe + \exp(Pe - Pe \cdot Z_0) \left[ 4/Pe - 4 Z_0/Pe \right. \\ & \left. - 4/Pe^2 \right] + \exp(-2 Z_0 Pe)/Pe^2 \\ & - \exp(2 Pe - 2 Z_0 Pe)/Pe^2 \dots \end{aligned} \quad (41)$$

If one considers the limit of the Case II moments as  $Z_0$  becomes very large, the two results are equivalent, or:

$$\lim_{Z_0 \rightarrow \infty} \mu_{1_{II}} = \mu_{1_I} = 1$$

and

$$\lim_{Z_0 \rightarrow \infty} \bar{\mu}_{2_{II}} = \bar{\mu}_{2_I} = 2/Pe$$

Table 3 summarizes the results of parameteric studies of the two moments considered for each case. The errors in Case II versus Case I moments for  $Z_0 = 1$  are significant for low Peclet number. The error diminishes with increasing Peclet number. This confirms the qualitative conclusions of Friedly (1972) for high values of  $Pe$ .

Table 3. Case I and Case II Comparison Results

Errors at $Z_0 = 1.0$						
Pe	Absolute Error ( $\mu_1 I - \mu_1 II$ )	Relative Error, % $\left( \frac{\mu_1 I - \mu_1 II}{\mu_1 I} \right) \times 100$	Absolute Error ( $\bar{\mu}_2 I - \bar{\mu}_2 II$ )	Relative Error, % $\left( \frac{\bar{\mu}_2 I - \bar{\mu}_2 II}{\bar{\mu}_2 I} \right) \times 100$	Safe $Z_0$ ( $\mu_1 I = \mu_1 II$ )*	Safe $Z_0$ ( $\bar{\mu}_2 I = \bar{\mu}_2 II$ )**
2	0.4323	43.23	1.245	124.5	9.791	11.768
4	0.2454	24.54	0.3125	62.9	5.254	6.021
8	0.1250	12.50	0.07813	31.2	3.043	3.328
16	0.06250	6.250	0.01953	15.6	1.978	2.073
32	0.03125	3.125	0.004883	7.91	1.467	1.490
64	0.01563	1.563	0.001221	3.91	1.223	1.222
128	0.00781	0.781	0.0003052	1.99	1.106	1.044
256	0.00391	0.391	0.0000763	0.976	1.050	1.002
512	0.00195	0.195	0.0000191	0.489	1.024	1.0005
1024	0.00098	0.098	0.0000047	0.241	1.011	1.0001
2048	0.00049	0.049	0.0000012	0.123	1.005	1.00002
4096	0.00024	0.024	0.0000003	0.0615	1.002	1.000005
8192	0.00012	0.012	0.0000000	0.0	1.001	1.000001

\*  $\mu_1 I - \mu_1 II \leq 10^{-8}$

\*\*  $\bar{\mu}_2 I - \bar{\mu}_2 II \leq 10^{-8}$

Table 3 also gives the value of  $Z_0$  which, when used in Case II, will yield output characteristics the same as Case I output characteristics. This means that for a given Peclet number, application of equation (33) at the noted  $Z_0$ , will yield output characteristics at  $Z=1$  that are, for all intents and purposes, the same as those predicted by Case I.

Table 4 presents some typical values of the Peclet parameter for several systems. For chromatographic systems, the range of the Peclet number is on the order of 5,000 to 10,000. Thus in this research, it appears that use of the zero-derivative condition (equation 33) at the column exit will not cause serious problems.

In conclusion, the comparison of the mean and variance for impulse responses at  $Z=1$  for the two different boundary conditions has yielded guidelines which are useful when approximating infinite column behavior using a finite terminal boundary condition. The use of the criteria for general pulse-type forcing functions would yield results wherein the absolute errors between the two cases would be the same but the relative errors between cases would decrease. The application of the results for models including other transport mechanisms ( $R_A \neq 0$ ) may be somewhat conservative. When applicable to more complicated models, the method of analysis used here will give more definite guidelines for each specific situation.

#### V. EVALUATION OF NUMERICAL TECHNIQUES - FINITE DIFFERENCE

This section and the one that follows present evaluations of two techniques which are available for the numerical solutions of the type of partial differential equation models that have been used and that



Table 4. Peclet Numbers for Four Typical Systems

<u>System</u>	<u>Pe</u>
Micro Gas Chromatograph Column (Water in Helium)	233
Typical Gas Chromatograph Column (Water in Helium)	5622
Typical Gas Dehydrator (Water in Helium)	1777
Small Experimental Reactor (SO <sub>2</sub> in Air)	155

are being postulated for the chromatographic system. The two methods considered are the Finite Difference method and the subclass of Weighted Residual methods known as Orthogonal Collocation.

#### Finite Difference Method

Finite difference approximations have predominantly been used in the analysis of partial differential equations. To obtain numerical solutions to partial differential equations, one replaces the continuous variables with discrete variables. The relations between these discrete variables in the method of finite differences are called finite difference equations. The relationships are based on Taylor series representations of the dependent variable. The domains of the independent variables that are discretized form a system of grid points. Figure 5 shows a grid representation for the transient analysis of a system with one spatial independent variable. The spatial dimension,  $Z$ , is shown as being bounded and the time variable,  $\theta$ , is shown with no particular bound. The grid is a fixed grid; i.e., spatial discretizations and time discretizations are uniform for each domain. Note that the value of  $Z$ , the continuous space dimension is given by:

$$Z = i \cdot (\Delta Z)$$

where  $i$  refers to a particular spatial grid point and  $\Delta Z$  is the spacing between spatial grid points. Similarly, the value of  $\theta$ , the continuous time variable is given by

$$\theta = j \cdot (\Delta \theta)$$

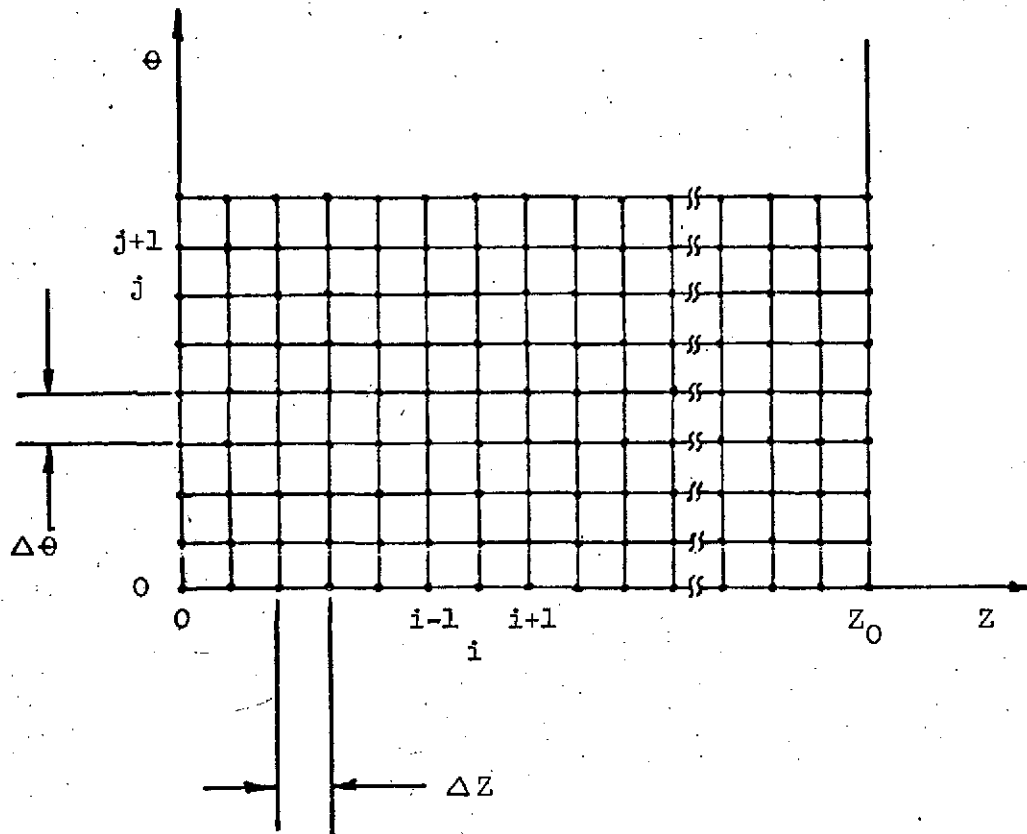


Figure 5. Grid Representation for Finite Difference Method

where  $j$  refers to a particular time grid point and  $\Delta \theta$  is the interval between time grid points.

For parabolic problems (as is the case for the second-order chromatograph system models), the two-level implicit method known as the Crank-Nicolson method is probably most popular and is well documented (Lapidus, 1962). In this method, the following approximations are made for the first and second spatial derivatives and the first time derivative:

$$(\partial y / \partial z)_{ij} \approx 1/2 \left[ \frac{y_{i+1,j} - y_{i-1,j}}{2 (\Delta z)} + \frac{y_{i+1,j+1} - y_{i-1,j+1}}{2 (\Delta z)} \right]$$

$$(\partial^2 y / \partial z^2)_{ij} \approx 1/2 \left[ \frac{y_{i+1,j} - 2y_{i,j} + y_{i-1,j}}{(\Delta z)^2} + \frac{y_{i+1,j+1} - 2y_{i,j+1} + y_{i-1,j+1}}{(\Delta z)^2} \right]$$

$$(\partial y / \partial \theta)_{ij} \approx (y_{i,j+1} - y_{i,j}) / \Delta \theta$$

where the  $i$  subscript denotes a coordinate in the spatial domain and the  $j$  subscript denotes a coordinate in the time domain.

Preliminary studies have been made applying the Crank-Nicolson method to the problem:

$$(1/Pe) (\partial^2 y / \partial z^2) - \partial y / \partial z = \partial y / \partial \theta$$

$$y(z, 0) = 0 \quad ; \quad z \geq 0$$

$$y(0, \theta) = \phi(\theta); \quad \theta > 0$$

$$\partial y(z_0, \theta) / \partial \theta = 0; \quad \theta > 0$$

Simulations were made with the following conditions.

1.  $\phi(\theta)$  was a triangular-type pulse of duration 0.01 and with unit area. This is quite a sharp pulse as far as typical chromatograph input pulses are concerned, but it was used mainly in the interest of saving computer time.
2. The Peclet number was fixed at 8,000.
3. The time increment,  $\Delta\theta$ , was held at 0.0004.
4. The response was studied at  $Z = 0.05$ . This is a drastic reduction in the normal spatial coordinate studied, but, again, this was done in the interest of conserving computer time.
5. The terminal boundary condition was applied at  $Z_0 = 0.20$ .
6. The spatial increment,  $\Delta Z$ , was varied in the following sequence:

0.0002, 0.0004, 0.0010, 0.0025

For spatial increment values of 0.0010 and less, the simulations were stable. However, when  $\Delta Z$  was increased to 0.0025, instability in the form of oscillation in the response was exhibited. The very small  $\Delta Z$  required is directly attributed to the  $Pe$  value used. This instable  $\Delta Z$  value is not quite as small as the value that is predicted by the stability criteria of Price, et. al. (1966).

The simulation for spatial increments of 0.0002, 0.0004, and 0.0010 gave reasonable results when compared to results convolving  $\phi(\theta)$  with the analytical impulse response. The discrepancy between

between the analytic and numerical computations appeared in the magnitudes of each response point - the numerical results were on the order of 20% too low. This in turn affected the area beneath the response curve for the numerical results - all areas were on the order of 0.80 as compared with the correct area of 1.0. The area under the analytical response curve was 0.96 which is tolerable considering the sharp input. This discrepancy in response area can be resolved by adding additional parameters to the difference equations to yield an exact conservative relationship (Rogers, 1973):

$$\left[ \begin{array}{l} \text{System Input - System Output over} \\ \text{the interval } j \text{ to } j + 1 \end{array} \right]$$

$$= \sum_{i=1}^N y_{i,j+1} - \sum_{i=1}^N y_{i,j}$$

where  $N$  is the total number of spatial points. This analysis was not performed because it was felt that the method already suffered from a more alarming feature - the high degree of spatial discretization which was necessary for the large  $Pe$  values encountered in chromatographic systems analysis. Extrapolation of the computing time required for the simulations performed yields an estimate of one to two hours of computer time required for complete simulations over the space interval  $(0, 1.0^+)$ . The time would naturally increase when broader input pulses are used. Similar conclusions on the use of finite difference schemes were reported earlier (Pfeiffer, 1972).

Because of the high degree of spatial discretization required by the finite difference method and the subsequent high cost of computer simulations, it is felt that further pursuit of finite difference formulations for problems similar to the above is not warranted at this time and that efforts must be directed to other methods.

#### VI. EVALUATION OF NUMERICAL TECHNIQUES - ORTHOGONAL COLLOCATION

A recent text (Finlayson, 1972) has dealt with several approximation techniques for the solution of the differential equations which arise in the analysis of transport phenomena. A group of approximation techniques has been designated the Method of Weighted Residuals (MWR). A subclass of MWR is the Method of Orthogonal Collocation. This method has been successfully applied to several problems in the realm of chemical reaction engineering. Investigators in this area include Ferguson and Finlayson (1970), Finlayson (1971), Villadsen and Stewart (1967), Villadsen and Sorensen (1969), and Villadsen (1970). The purpose of this section is to present a summary of the theory behind the method and to discuss investigations that have been made relative to its applicability to the types of problems that must be solved in conjunction with the modelling of the chromatographic system.

##### A. Theory and Background

The Method of Weighted Residuals approach to the solution of partial differential equations starts with a representation of the dependent variable,  $y$ , by a finite sum of trial functions  $P_i$ . An example might be:

$$y(z, \theta) \approx \phi_0(z, \theta) + \sum_{i=1}^N a_i(\theta) P_{i-1}(z) \quad (42)$$

where  $\phi_0(z, \theta)$  is a function which may be chosen to satisfy one or more boundary conditions. The functions  $P_i(z)$  are normally specified and the time-varying coefficients,  $a_i(\theta)$ , are determined in a manner to give the "best" solution of the differential equation.

The next step in the MWR is to manipulate the differential equation such that one side, say the right hand side, of the equation is zero. Then, the trial function expansion is substituted into the left hand side. This substitution of the trial function expansion into the manipulated differential equation forms what is termed the residual, Res. If the trial function were exact, the residual would be zero. In MWR, the coefficients,  $a_i(\theta)$  are determined by specifying weighted integrals of the residual to be zero; i.e.,

$$\int_V W_j(\text{Res}) dV = 0 \quad ; \quad j = 1, 2, \dots, N \quad (43)$$

The choice of weighting functions,  $W_j$ , determines what class of MWR is to be applied. For the general collocation method, the weighting functions are chosen as displaced Dirac delta functions:

$$W_j = \delta(z - z_j) \quad ; \quad j = 1, 2, \dots, N \quad (44)$$

Substitution of equation (44) into equation (43) gives the result of forcing the residual to be zero at  $N$  specified collocation points.

As the degree of approximation is increased, the residual will be forced



to be zero at an increasing number of points in the spatial domain and the trial function should converge to the true solution within a given accuracy.

Within the class of collocation methods is the subclass of orthogonal collocation. The distinguishing feature of this method is that the trial functions,  $P_i(Z)$ , are chosen as orthogonal polynomials defined by the following relationship:

$$\int_a^b W(Z) P_i(Z) P_j(Z) dZ = C_i \delta_{ij} \quad (45)$$

where  $[a, b]$  is the interval of orthogonality,  $W(Z)$  is a positive weighting function on  $[a, b]$ ,  $C_i$  is a scale factor, and  $\delta_{ij}$  is the Kronecker delta. The group of polynomials defined by equation (44) is said to be orthogonal on the interval  $[a, b]$  with respect to the weighting function  $W(Z)$ .

The  $N$  collocation points are chosen as roots to  $P_N'(Z)$ , which is the polynomial of the next highest order in the trial function expansion, the highest being  $P_{N-1}$  in equation (42). The basis for choosing the roots of the polynomial as the collocation points instead of equidistant points in the interval of interest can be found in the theory of polynomial interpolation. Several results, as documented by Lanczos (1956) are summarized here:

1. Polynomial expansions are justified due to the fundamental theorem proved by Weierstrass in 1885 which establishes that any continuous function in a finite interval can always be approximated to any degree of accuracy by finite power series.

2. The Weierstrass theorem does not imply that an approximating polynomial can be obtained by using equidistant points. This behavior was studied by Runge in 1901 who showed that equidistant interpolation of some very simple analytical functions could in certain regions yield very erroneous results which did not disappear with increased points. This behavior is termed the "Runge phenomenon."
3. The difficulties which occur with equidistant interpolation disappear when the zeros of the first neglected polynomial in the polynomial approximation are used as interpolation points. However, this introduces the need to know the roots of the particular polynomial.

B. Problem Formulation Using Orthogonal Collocation

The solution of parabolic partial differential equations using orthogonal collocation requires several steps which are independent of the particular equation under consideration. This section presents two formulations which are theoretically equivalent but which differ in computational and coding advantages. The first formulation, although somewhat more complex from a coding point of view, will be shown to be superior for computations.

A trial function has been proposed, Finlayson (1972, p. 105), for second order systems on the spatial interval  $[0, 1]$ . For transient analysis, the trial function is of the form:

$$y(Z, \theta) = f(\theta) + g(\theta)Z + Z(1-Z) \sum_{i=1}^N a_i(\theta) P_{i-1}(Z) \quad (46)$$

The above equation has  $N+2$  unknowns: the functions  $f(\theta)$ ,  $g(\theta)$  and  $\{a_i(\theta)\}$ ,  $i=1, N$ . These are determined by the boundary conditions at  $Z=0$  and  $Z=1$  and by performing collocation at the  $N$  roots of  $P_N(Z)$ .

Thus, one has a set of  $N+2$  points:

$$Z_1 = 0$$

$$Z_{N+2} = 1$$

and  $\{Z_j\}$ ;  $j=2, N+1$ ; the roots of  $P_N(Z)$ .

Now, if one were to construct the approximate solution at these  $N+2$  points, a matrix equation would result:

$$\begin{bmatrix} y(Z_1, \theta) \\ y(Z_2, \theta) \\ \vdots \\ y(Z_{N+1}, \theta) \\ y(Z_{N+2}, \theta) \end{bmatrix} = \begin{bmatrix} 1 & Z_1 & Z_1(1-Z_1)P_0(Z_1) & \dots & Z_1(1-Z_1)P_{N-1}(Z_1) \\ 1 & Z_2 & Z_2(1-Z_2)P_0(Z_2) & \dots & Z_2(1-Z_2)P_{N-1}(Z_2) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 1 & Z_{N+1} & Z_{N+1}(1-Z_{N+1})P_0(Z_{N+1}) & \dots & Z_{N+1}(1-Z_{N+1})P_{N-1}(Z_{N+1}) \\ 1 & Z_{N+2} & Z_{N+2}(1-Z_{N+2})P_0(Z_{N+2}) & \dots & Z_{N+2}(1-Z_{N+2})P_{N-1}(Z_{N+2}) \end{bmatrix} \begin{bmatrix} f(\theta) \\ g(\theta) \\ a_1(\theta) \\ \vdots \\ a_N(\theta) \end{bmatrix} \quad (47)$$

Now define the following quantities:

$$\underline{y} \triangleq \begin{bmatrix} y(Z_1, \theta) \\ y(Z_2, \theta) \\ \vdots \\ y(Z_{N+1}, \theta) \\ y(Z_{N+2}, \theta) \end{bmatrix} \quad (48)$$

$$\underline{R} \stackrel{\Delta}{=} \begin{bmatrix} 1 & z_1 & z_1(1-z_1)P_0(z_1) & \dots & z_1(1-z_1)P_{N-1}(z_1) \\ 1 & z_2 & z_2(1-z_2)P_0(z_2) & \dots & z_2(1-z_2)P_{N-1}(z_2) \\ \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & & \cdot \\ 2 & z_{N+1} & z_{N+1}(1-z_{N+1})P_0(z_{N+1}) & \dots & z_{N+1}(1-z_{N+1})P_{N-1}(z_{N+1}) \\ 1 & z_{N+2} & z_{N+2}(1-z_{N+2})P_0(z_{N+2}) & \dots & z_{N+2}(1-z_{N+2})P_{N-1}(z_{N+2}) \end{bmatrix} \quad (49)$$

$$\underline{f} \stackrel{\Delta}{=} \begin{bmatrix} f(\theta) \\ g(\theta) \\ a_1(\theta) \\ \cdot \\ \cdot \\ \cdot \\ a_N(\theta) \end{bmatrix} \quad (50)$$

Use of equations (48), (49) and (50) reduces equation (47) to the more compact form:

$$\underline{y} = \underline{R} \underline{f} \quad (51)$$

The spatial derivatives may be expressed in a similar form:

$$\frac{\partial \underline{y}}{\partial z} = \underline{R} \underline{1} \underline{f} \quad (52)$$

$$\frac{\partial^2 \underline{y}}{\partial z^2} = \underline{R} \underline{2} \underline{f} \quad (53)$$

where

$$\frac{\partial y}{\partial z} \Delta = \begin{bmatrix} \partial y(z_1, \theta) / \partial z \\ \partial y(z_2, \theta) / \partial z \\ \vdots \\ \partial y(z_{N+1}, \theta) / \partial z \\ \partial y(z_{N+2}, \theta) / \partial z \end{bmatrix} \quad (54)$$

$$\frac{\partial^2 y}{\partial z^2} \Delta = \begin{bmatrix} \partial^2 y(z_1, \theta) / \partial z^2 \\ \partial^2 y(z_2, \theta) / \partial z^2 \\ \vdots \\ \partial^2 y(z_{N+1}, \theta) / \partial z^2 \\ \partial^2 y(z_{N+2}, \theta) / \partial z^2 \end{bmatrix} \quad (55)$$

$$[R1] \quad j, 1 = 0 \quad ; \quad j = 1, N+2$$

$$[R1] \quad j, 2 = 1 \quad ; \quad j = 1, N+2 \quad (56)$$

$$[R1] \quad j, i = z_j(1-z_j) \frac{\partial P_{i-3}(z_j)}{\partial z} + (1-2z_j) P_{i-3}(z_j); \quad j = 1, N+2 \\ i = 3, N+2$$

and

$$\left. \begin{aligned}
 [R2] \quad j,1 &= [R2] \quad j,2 = 0 \quad ; \quad j = 1, N+2 \\
 [R2] \quad j,i &= Z_j(1-Z_j) \frac{\partial^2 P_{i-3}(Z_j)}{\partial Z^2} + 2(1-2Z_j) \frac{\partial P_{i-3}(Z_j)}{\partial Z} \\
 &\quad - 2 P_{i-3}(Z_j); \quad j = 1, N+2 \\
 &\quad i = 3, N+2
 \end{aligned} \right\} \quad (57)$$

The time-varying vector  $\underline{f}$  may be eliminated from equations (52) and (53) by premultiplying equation (51) by the inverse of  $\underline{R}$ ,  $\underline{R}^{-1}$ , or:

$$\underline{f} = \underline{R}^{-1} \underline{y}$$

and

$$\frac{\partial \underline{y}}{\partial Z} = \underline{R1} \quad \underline{R}^{-1} \quad \underline{y} \quad (58)$$

$$\frac{\partial^2 \underline{y}}{\partial Z^2} = \underline{R2} \quad \underline{R}^{-1} \quad \underline{y} \quad (59)$$

Equations (58) and (59) thus yield expressions for the first and second spatial derivatives at the  $N+2$  points in terms of the solution at the  $N+2$  points.

Alternative to the formulation of above is a formulation which is presented by Finlayson (1972, pp. 105-106). Expansion of equation (46) yields an  $(N+1)$  order polynomial:

$$y(Z, \theta) = f(\theta) + \sum_{i=1}^{N+1} d_i(\theta) Z^i \quad (60)$$

Writing the approximate solution at the  $N+2$  points yields a matrix equation similar to equation (51):

$$\underline{y} = \underline{Q} \underline{d} \quad (61)$$

where:

$$\underline{Q} \triangleq \begin{bmatrix} 1 & z_1 & z_1^2 & \dots & z_1^{N+1} \\ 1 & z_2 & z_2^2 & \dots & z_2^{N+1} \\ \vdots & \vdots & \vdots & & \vdots \\ 1 & z_{N+1} & z_{N+1}^2 & \dots & z_{N+1}^{N+1} \\ 1 & z_{N+2} & z_{N+2}^2 & \dots & z_{N+2}^{N+1} \end{bmatrix} \quad (62)$$

$$\underline{d} \triangleq \begin{bmatrix} f(\theta) \\ d_1(\theta) \\ d_2(\theta) \\ \vdots \\ d_{N+1}(\theta) \end{bmatrix} \quad (63)$$

The first and second spatial derivative vectors can be written as:

$$\frac{\partial y}{\partial z} = \underline{Q1} \underline{d} \quad (64)$$

and

$$\frac{\partial^2 y}{\partial z^2} = \underline{Q2} \underline{d} \quad (65)$$

where

$$[Q1]_{ji} = (i-1) z_j^{i-2} ; \quad \begin{matrix} j=1, N+2 \\ i=1, N+2 \end{matrix} \quad (66)$$

$$[Q2]_{ji} = (i-1)(i-2) z_j^{i-3} ; \quad \begin{matrix} j=1, N+2 \\ i=1, N+2 \end{matrix} \quad (67)$$

As in the first formulation, the time-varying vector,  $\underline{d}$ , may be eliminated from equations (64) and (65) by pre-multiplying equation (61) by the inverse of  $\underline{Q}$ ,  $\underline{Q}^{-1}$ , or:

$$\underline{d} = \underline{Q}^{-1} \underline{y}$$

and

$$\frac{\partial \underline{y}}{\partial z} = \underline{Q1} \underline{Q}^{-1} \underline{y} \quad (68)$$

$$\frac{\partial^2 \underline{y}}{\partial z^2} = \underline{Q2} \underline{Q}^{-1} \underline{y} \quad (69)$$

Thus, equations (68) and (69) give expressions which are identical to equations (58) and (59). The matrix product  $\underline{R1} \underline{R}^{-1}$  is equivalent to  $\underline{Q1} \underline{Q}^{-1}$  and  $\underline{R2} \underline{R}^{-1}$  is equivalent to  $\underline{Q2} \underline{Q}^{-1}$ . Since the computations of  $\underline{Q}$ ,  $\underline{Q1}$ , and  $\underline{Q2}$  only require knowledge of the collocation points and not the knowledge of the particular polynomial coefficients being considered, one might conceivably prefer the second formulation. Both formulations require the computation of the inverse of an  $(N+2)$  square matrix.



Computationally, it is desirable for the matrix being inverted to be well-conditioned with respect to inversion. An analysis has been made comparing the inversion qualities of the matrices  $\underline{R}$  and  $\underline{Q}$ . The ease of inversion is measured by the condition number of  $\underline{R}$  and  $\underline{Q}$  respectively and with the number of decimal digits which are left unchanged following iterative improvement of the initial Gauss-Jordan reduction of each matrix. Stewart (1973) discusses the problem of ill-conditioning and the use of iterative improvement in matrix inversion. Table 5 compares the inversion characteristics of  $\underline{R}$  and  $\underline{Q}$  for increasing  $N$ . The condition numbers cited are lower bounds on the true condition numbers relative to the  $L_1$  norm.\* Appendix F shows how the lower bound and the upper bound on the condition number is computed. Except in the analysis of  $\underline{Q}$  for  $(N+2) \geq 22$ , there were no practical differences in the lower and upper bounds.

Table 5 indicates that the matrix  $\underline{R}$  is well-conditioned with respect to inversion using the double-precision word length available on the IBM 360/50 computer. In all cases, the computation of the product  $\underline{R} \underline{R}^{-1}$  yielded a matrix whose off-diagonal elements were less than or equal to  $10^{-16}$ . The table also shows the progressively poorer conditioning of  $\underline{Q}$  with respect to inversion. The (26 x 26) case is so ill-conditioned that inversion using the available computer

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\* The  $L_1$  norm of an  $(n \times n)$  matrix  $A$  is defined as:

$$L_1 \text{ norm } (A) \triangleq \max_j \left( \sum_{i=1}^n |A_{ij}| \right); j=1, 2, \dots, n$$

Table 5. Comparison of Conditioning of  $\underline{R}$  and  $\underline{Q}$  Matrices with Respect to Inversion

Matrix Size	Lower Bound on Condition of $\underline{R}$	IDGT $^*_R$	Lower Bound on Condition of $\underline{Q}$	IDGT $^*_Q$
( 3 x 3 )	$0.120 \times 10^2$	15	$0.240 \times 10^2$	15
( 4 x 4 )	$0.328 \times 10^2$	15	$0.149 \times 10^3$	15
( 5 x 5 )	$0.739 \times 10^2$	15	$0.944 \times 10^3$	15
( 6 x 6 )	$0.142 \times 10^3$	15	$0.591 \times 10^4$	14
( 7 x 7 )	$0.243 \times 10^3$	15	$0.366 \times 10^5$	14
( 8 x 8 )	$0.384 \times 10^3$	15	$0.225 \times 10^6$	13
( 9 x 9 )	$0.571 \times 10^3$	15	$0.138 \times 10^7$	13
(10 x 10)	$0.812 \times 10^3$	15	$0.840 \times 10^7$	11
(11 x 11)	$0.111 \times 10^4$	15	$0.510 \times 10^8$	11
(12 x 12)	$0.148 \times 10^4$	15	$0.309 \times 10^9$	11
(14 x 14)	$0.244 \times 10^4$	15	$0.112 \times 10^{11}$	9
(18 x 18)	$0.545 \times 10^4$	15	$0.145 \times 10^{14}$	6
(22 x 22)	$0.103 \times 10^5$	15	$0.177 \times 10^{17}$	2
(26 x 26)	$0.179 \times 10^5$	15	$0.907 \times 10^{18}$	0**

\* IDGT is the approximate number of digits in the inverse which were left unchanged after iterative improvement.

\*\* There was no convergence in the iterative improvement. The upper bound on the condition of  $\underline{Q}$  was  $0.202 \times 10^{39}$  based on the "best"  $\underline{Q}^{-1}$ .

Note: Subscripts R and Q on IDGT refer to inversion of  $\underline{R}$  and  $\underline{Q}$  respectively.

is computationally impossible. Based on condition numbers and accuracy, either formulation is acceptable for  $(N+2) \leq 5$ ; while for  $(N+2) > 6$ , the first formulation is preferable.

It should be noted that Finlayson (1972, p. 35) alludes to this problem in his text but the comment is quite qualitative and somewhat obscure:

"The orthogonality of the polynomials gives computational advantages, although the same approximation can be expressed in terms of powers of  $x$ , if the computations can be done accurately enough."

The preceding analysis used the roots of the so-called shifted Legendre polynomials. These are defined by equation (45) if one lets  $a = 0$ ,  $b = 1$  and  $w(Z) = 1$ . The polynomial coefficients were computed using the relationships of Villadsen (1970). Figure 6 shows the behavior of the first four of these polynomials. The roots were computed by shifting the abscissas from Gaussian quadrature formulae, available in Abramowitz and Segun (1965), Love (1966), and Stroud and Secrest (1966).

Although most of the problems solved by others using orthogonal collocation have not required over 12 collocation points, the results of this section point out a computation disadvantage of the second formulation which appears at a fairly small degree of discretization and which gets progressively worse. The first formulation requires some additional information but successfully circumvents the problems inherent in the second formulation.

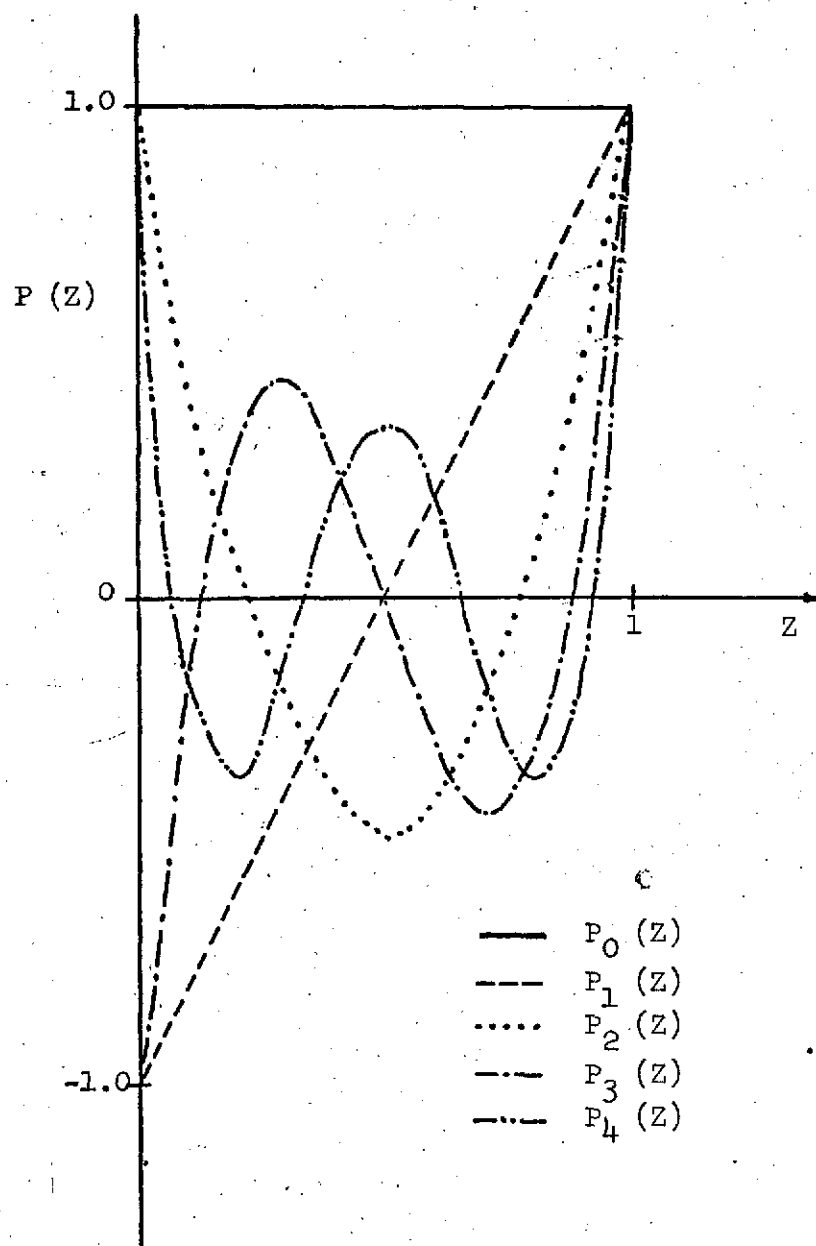


Figure 6. Shifted Legendre Polynomials of Order Zero to Four

### C. Sample Application of Orthogonal Collocation

The preceding can be applied to illustrate how a partial differential equation of the type encountered in chromatographic systems analysis can be solved. The same example will be used (except for the forcing function) as was considered in the evaluation of the finite difference technique the problem is:

$$(1/Pe) (\partial^2 y / \partial Z^2) - \partial y / \partial Z = \partial y / \partial \theta$$

$$y(Z, 0) = 0$$

$$y(0, \theta) = \phi(\theta) ; \theta > 0$$

$$\partial y(Z_0, \theta) / \partial Z = 0 ; \theta > 0$$

The preceding analysis has been conducted based on the spatial interval of  $[0, 1]$  as the interval of orthogonality for the orthogonal polynomials used in the trial function expansion. However, as was shown in Section IV,  $Z_0$  should be different from unity depending on the value of the Peclet number. To avoid the derivation of additional polynomials orthogonal on an interval  $[0, Z_0]$  and the determination of the required roots, the above problem may be rescaled in the spatial domain by the following change in variable:

$$Z_{\text{new}} = (1/Z_0) Z$$

Therefore:

$$1/\partial Z = (1/Z_0) 1/\partial Z_{\text{new}} \quad (70)$$

$$(1/\partial Z)^2 = (1/Z_0)^2 (1/\partial Z_{\text{new}})^2$$

Use of equations (70) and (71) and deletion of the subscript "new" yields the re-scaled problem:

$$\left(\frac{1}{Pe}\right) \left(\frac{1}{Z_0}\right)^2 (\partial^2 y / \partial Z^2) - \left(\frac{1}{Z_0}\right) (\partial y / \partial Z) = \partial y / \partial \theta \quad (72)$$

$$y(Z, 0) = 0 \quad (73)$$

$$y(0, \theta) = \phi(\theta) \quad ; \quad \theta > 0 \quad (74)$$

$$\partial y(1, \theta) / \partial Z = 0 \quad ; \quad \theta > 0 \quad (75)$$

Where one was concerned about the dimensionless length of unity in the old coordinate system, one is now concerned with the dimensionless length of  $(1/Z_0)$  which now corresponds to the outlet of the bed.

One can now apply the matrices given in equations (58) and (59) to yield a set of coupled, ordinary differential equations. Since one requires the partial differential equation to be satisfied at the  $N$  collocation points, the result is  $N$  coupled ordinary differential equations. If

$$[W]_{ji} \triangleq \left(\frac{1}{Pe}\right) \left(\frac{1}{Z_0}\right)^2 [\underline{R2} \quad \underline{R}^{-1}]_{ji} - \left(\frac{1}{Z_0}\right) [\underline{R1} \quad \underline{R}]_{ji} ; \quad (76)$$

$$i = 1, N+2 ; \quad j = 1, N+2$$

then

$$\frac{d y_j}{d \theta} = \sum_{i=1}^{N+2} [W]_{ji} y_i \quad ; \quad j = 2, N+1 \quad (77)$$

Application of the boundary conditions yield:

$$y_1 = y(Z, \theta) = f(\theta) = \phi(\theta) \quad (78)$$

and

$$0 = \sum_{i=1}^{N+2} \begin{bmatrix} \underline{R1} & \underline{R}^{-1} \end{bmatrix}_{N+2,i} y_i \quad (79)$$

Using equation (79) one may solve for  $y_{N+2}$  ( $=y(Z_{N+2}, \theta)$ ):

$$y_{N+2} = \frac{\sum_{i=2}^{N+1} \begin{bmatrix} \underline{R1} & \underline{R}^{-1} \end{bmatrix}_{N+2,i} y_i}{\begin{bmatrix} \underline{R1} & \underline{R}^{-1} \end{bmatrix}_{N+2, N+2}} - \frac{\begin{bmatrix} \underline{R1} & \underline{R}^{-1} \end{bmatrix}_{N+2,1} y_1}{\begin{bmatrix} \underline{R1} & \underline{R}^{-1} \end{bmatrix}_{N+2, N+2}} \quad (80)$$

Equations (78) and (80) can further be used to reduce equation (77) to:

$$\begin{aligned} \frac{d y_j}{d \theta} = & \sum_{i=2}^{N+1} \left\{ \begin{bmatrix} W \end{bmatrix}_{ji} - \frac{\begin{bmatrix} W \end{bmatrix}_{j,N+2} \begin{bmatrix} \underline{R1} & \underline{R}^{-1} \end{bmatrix}_{N+2,i}}{\begin{bmatrix} \underline{R1} & \underline{R}^{-1} \end{bmatrix}_{N+2,N+2}} \right\} y_i \\ & + \left\{ \begin{bmatrix} W \end{bmatrix}_{j,1} - \frac{\begin{bmatrix} W \end{bmatrix}_{j,N+2} \begin{bmatrix} \underline{R1} & \underline{R}^{-1} \end{bmatrix}_{N+2,1}}{\begin{bmatrix} \underline{R1} & \underline{R}^{-1} \end{bmatrix}_{N+2,N+2}} \right\} \phi(\theta) \\ & ; \quad j = 2, N+1 \end{aligned} \quad (81)$$

Now, define the following quantities:

$$\underline{Y} \triangleq \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_N \end{bmatrix} = \begin{bmatrix} y_2 \\ y_3 \\ \vdots \\ y_{N+1} \end{bmatrix} \quad (82)$$

$$\dot{\underline{Y}} \triangleq \begin{bmatrix} d y_1 / d \theta \\ \vdots \\ d y_N / d \theta \end{bmatrix} \quad (83)$$

$$[A]_{ji} \triangleq [W]_{j+1, i+1} - [W]_{j+1, N+2} [\underline{R1} \quad \underline{R}^{-1}]_{N+2, i+1} /$$

$$[\underline{R1} \quad \underline{R}^{-1}]_{N+2, N+2} ; i=1, N ; j=1, N \quad (84)$$

$$[b]_j \triangleq [W]_{j+1, 1} - [W]_{j+1, N+2} [\underline{R1} \quad \underline{R}^{-2}]_{N+2, 1} /$$

$$[\underline{R1} \quad \underline{R}^{-1}]_{N+2, N+2} ; j=1, N \quad (85)$$

Equations (82) through (85) may now replace equation (81)

by:

$$\dot{\underline{Y}} = \underline{A} \underline{Y} + \underline{b} \phi(\theta) \quad (86)$$

Thus, one has reduced the distributed system to a lumped system via the spatial discretization given by application of the orthogonal collocation



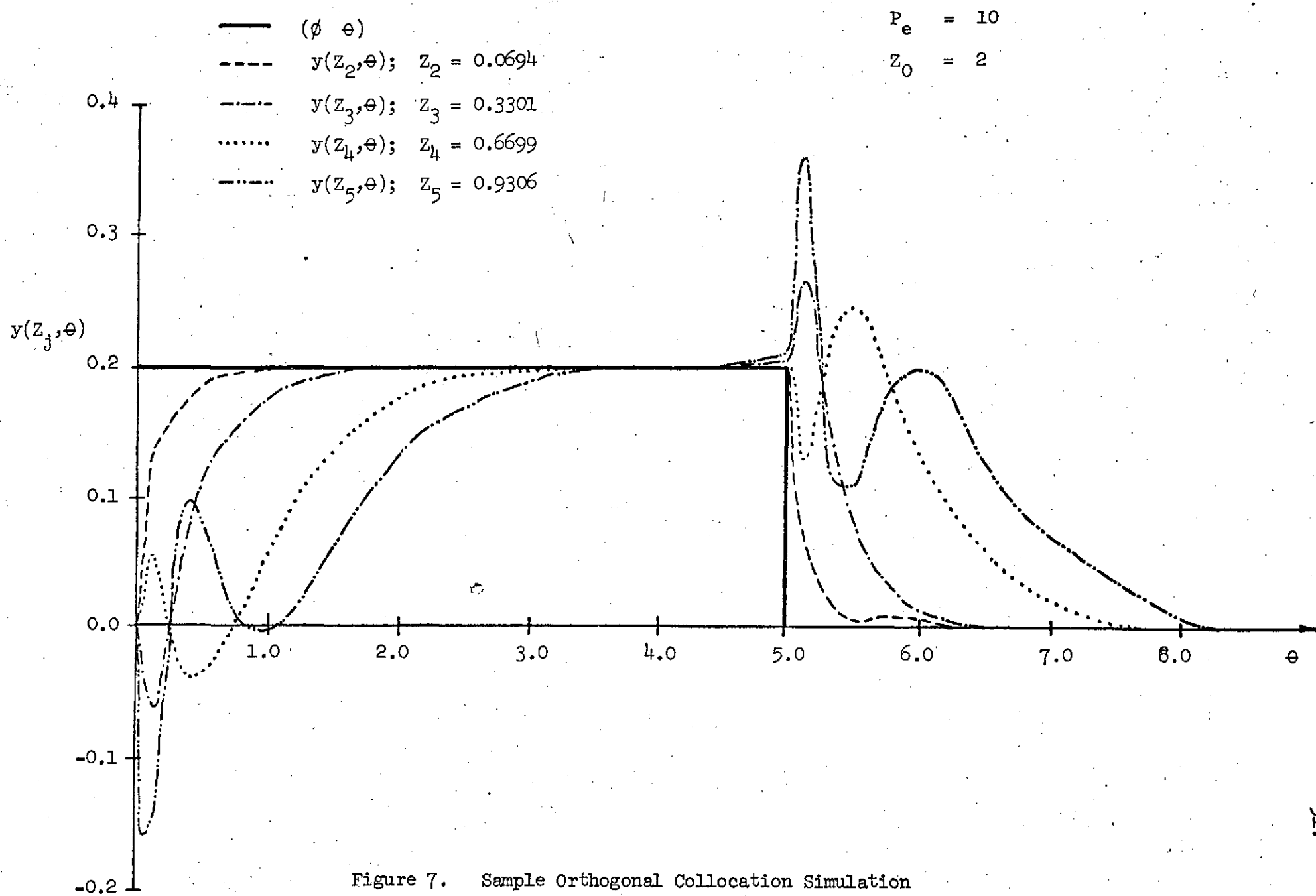
method. Equation (86) is a general form for a forced, linear system of ordinary differential equations. The stability of the system is determined solely by the characteristic values or eigenvalues of the system matrix  $\underline{A}$ .

An eigenanalysis was made of  $\underline{A}$  for Peclet numbers of 1, 10, 100, 1000, and 10,000. The number of collocation points,  $N$ , was varied in the sequence 4, 8, 12, 16, 20, and 24. The shifted Legendre polynomials and roots were used in the analysis. The value of  $Z_0$  was held at 2 for all cases.

For the cases of  $Pe$  of 10, 100, 1000, and 10,000, the eigenanalysis yielded eigenvalues with negative real parts or the calculation was stable. For the cases of a  $Pe$  of 1 and all  $N$ , there was a least one eigenvalue with a positive real part, revealing an unstable computational method.

While stability is indicated by the negative real parts of the eigenvalues, an oscillatory behavior was indicated by the presence of imaginary parts for a majority of the eigenvalues in each case. Prior to this eigenanalysis, some simulations had been made which exhibited damped oscillation in response to  $\phi(\theta)$  being a unit rectangular pulse. Additional simulations were performed after the eigenanalysis with similar oscillations noted in the responses at the collocation points. Figure 7 shows a simulation for  $N=4$ ,  $Z_0=2$  and  $Pe=10$ . The forcing function,  $\phi(\theta)$ , is a unit rectangular pulse of duration 5.0 dimensionless time units. The value of the response at  $Z = 1/Z_0$  is interpolated by the formula:

$$y(1/Z_0, \theta) = \underline{r}^T \underline{R}^{-1} \underline{y} \quad (87)$$



where:

$$\underline{r} \triangleq \begin{bmatrix} 1 \\ (1/Z_0) \\ (1/Z_0) (1 - 1/Z_0) P_0 (1/Z_0) \\ (1/Z_0) (1 - 1/Z_0) P_1 (1/Z_0) \\ \vdots \\ (1/Z_0) (1 - 1/Z_0) P_{N-1} (1/Z_0) \end{bmatrix} \quad (88)$$

While the simulation appears adequate for long-time dynamics, it appears inadequate for short-time dynamic situations which are in the pulsed chromatographic system.

It is concluded that the trial function proposed for work in axial-diffusion may be adequate for steady-state analysis and for long-time dynamic analysis of systems forced by inputs such as step functions. The next section presents ideas as to how a different trial function expansion may give better results for the short-time dynamics prevalent in the pulsed chromatographic system.

#### D. Use of Orthogonal Collocation in Chromatographic System Modelling

The results of the previous section have forced consideration of a trial function which may be more adequate for purposes of the dynamic analysis of the pulsed chromatographic system. For the problem considered in section VI.C., an alternative trial function

expansion is proposed which may be more suitable for the pulsed system.

It is:

$$y(Z, \theta) = f(\theta - Z) + g(\theta) Z + Z(1-Z) \sum_{i=1}^N a_i(\theta) P_{i-1}(Z)$$

The difference from the previous trial function form resides in the first term of the trial function,  $f(\theta - Z)$ . At  $Z=0$ , this is just  $f(\theta)$  or  $\phi(\theta)$ , the input wave. At subsequent axial positions, the trial function is the translated input plus some additional terms to "correct" for the axial diffusion. This analysis corresponds to the situation where  $Pe = \infty$ . A hyperbolic problem results with the analytic solution:

$$y(Z, \theta) = \phi(\theta - Z)$$

From the problem of diffusion and convection alone, this function included in the trial function should yield a response with a correct mean since the mean of the response is unaffected by the diffusive term.

Use of this type of trial function revision is presently being studied. It is thought that results obtained by using this revised trial function will be more favorable than the results obtained using equation (46).

## VII. CONCLUSIONS AND FUTURE WORK

This report has summarized work conducted during the period June 1972 through August 1973. The work has dealt with the area of chromatographic systems study referred to as Model Improvement.

Previous work dictated the formulation of a model which took into account more of the dynamically relevant transport mechanisms. A model has been formulated which includes intraparticle diffusion and rates of adsorption that were heretofore neglected. The model has been analysed using the moment analysis technique. This analysis of the proposed Inter-Intraparticle Adsorption Model indicates that the gross characteristics of actual data are more adequately predicted than with previous models.

The mathematical complexity of the proposed Inter-Intraparticle Adsorption Model has prompted consideration of numerical techniques appropriate for the solution of the partial differential equation models which are being postulated. The use of numerical techniques for the second-order models being considered requires the use of a finite terminal boundary condition. Criteria have been developed for a simple model wherein a finite terminal boundary condition can be applied which yields system responses which are for all intents and purposes equivalent to the responses obtained using an infinite column boundary condition.

Investigations into the merits of the more popular Finite Difference Technique for solutions to partial differential equations of the type encountered in chromatographic modelling have concluded that their use is not warranted because of the large degree of spatial discretization required for numerical stability. This drawback forces the use of a large amount of computer time to perform simulations.

Investigations into the merits of the method of Orthogonal Collocation as applied to the solution of partial differential equations of the type encountered in chromatograph system models has resulted in some inadequate results. However, the results are based on a trial function expansion which is more suitable for steady-state system analysis. The use of a modified trial function should give results which better model the dynamics of the system.

Future work in the area of chromatograph system modelling will deal with the establishment of a reliable and efficient technique for the numerical solution of the chromatograph model equations such that the dynamic effects of the added transport mechanisms, which prohibit analytic solutions, may be adequately studied and analysed.

#### VIII. ACKNOWLEDGEMENT

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IX. NOMENCLATURE

- $A_\delta$  - unit impulse, Dirac delta function.
- $\underline{A}$  - system matrix defined by equation (84).
- $A_Y, A_X, A_G$  - areas under output response curve, input response curve, and impulse response curve, respectively.
- $a$  - lower bound of interval of orthogonality used in orthogonal polynomial definition, equation (45).
- $a_i(\theta)$  - time-varying coefficients in trial function expansion.
- $a_p$  - ratio of interfacial area to packed volume.
- $b$  - upper bound of interval of orthogonality used in orthogonal polynomial definition, equation (45).
- $\underline{b}$  - forcing function vector defined in equation (85).
- $c_i$  - scale factor used in orthogonal polynomial definition, equation (45).
- $d_i(\theta)$  - time varying coefficients in trial function expansion.
- $\underline{d}$  - vector of time-varying coefficients defined in equation (63).
- $f(\theta)$  - time-varying function in the trial function expansion.
- $\underline{f}$  - vector of time-varying coefficients defined in equation (50).
- $g(\theta)$  - time-varying function in the trial function expansion.

- $L$  - length of chromatograph column.
- $M$  - equilibrium constant.
- $N$  - number of collocation points.
- $N_{RU}$  - the number of reactor units, a dimensionless measure of the rate of adsorption.
- $N_{toG}$  - number of transfer units, dimensionless.
- $Pe$  - Peclet number, dimensionless.
- $Pe_A$  - intraparticle Peclet number, a dimensionless measure of diffusion rates within the particle.
- $Pe_E$  - interparticle Peclet number, a dimensionless measure of diffusion rates within the carrier gas.
- $P_i(z)$  - group of polynomials, initially arbitrary but later constrained to be orthogonal on interval  $[a, b]$  by equation (45).
- $\underline{Q}$  - matrix defined by equation (62).
- $\underline{Q1}$  - matrix defined by equation (66).
- $\underline{Q2}$  - matrix defined by equation (67).
- $r$  - intraparticle space variable, dimensionless.
- $\underline{r}$  - vector defined by equation (88).
- $R$  - particle radius.
- $R_A$  - rate of sample adsorption.
- $R_I$  - moles of fluid in particle per mole of adsorption sites.
- $R_O$  - moles of fluid within the total bed per moles of adsorption sites within the bed.



- $\underline{R}$  - matrix defined by equation (49).
- $\underline{R1}$  - matrix defined by equation (56).
- $\underline{R2}$  - matrix defined by equation (57).
- Res - residual formed by trial function substitution  
in a differential equation.
- s - Laplace transform variable.
- $W(Z)$  - weighting function used in orthogonal polynomial  
defining equation (45).
- $W_j$  - weighting function in weighted residual integral,  
equation (43).
- $\underline{W}$  - matrix defined by equation (76).
- $x_a$  - adsorbed phase concentration, dimensionless.
- y - interparticle gas phase composition, dimensionless.
- $y_i$  - intraparticle gas phase composition, dimensionless.
- $y_i^*$  - equilibrium intraparticle gas phase composition,  
dimensionless.
- $\underline{y}$  - vector defined by equation (48).
- $\underline{Y}$  - vector defined by equation (82).
- $\underline{\dot{Y}}$  - vector defined by equation (83).
- Z - axial position in column, dimensionless.
- $Z_j$  - collocation point or end point, dimensionless.
- $Z_0$  - axial position where finite terminal boundary  
condition, equation (33), is applied.

GREEK LETTERS

- $\beta$  - particle porosity or void fraction.  
 $\Delta t$  - time increment in finite difference method.  
 $\Delta z$  - space increment in finite difference method.  
 $\delta ( )$  - Dirac delta function.  
 $\delta_{ij}$  - Kronecher delta  
 $\epsilon$  - void fraction of the bed.  
 $\theta$  - dimensionless time variable.  
 $\mu_n$  - the  $n^{\text{th}}$  moment about the origin defined by equation (14).  
 $\bar{\mu}_n$  - the  $n^{\text{th}}$  moment about  $\mu_1$ , defined by equation (17).  
 $\phi_0$  - function which satisfied boundary condition in trial function expansion.

SUBSCRIPTS

- I - refers to Case I boundary condition analysis.  
 II - refers to Case II boundary condition analysis.  
 i - refers to space level in Finite Difference technique; refers to column in Orthogonal Collocation matrices.  
 j - refers to time level in Finite Difference techniques; refers to row and/or collocation point in Orthogonal Collocation matrices.

MISCELLANEOUS

- $[ ]_{ji}$  - refers to the matrix element of the  $j^{\text{th}}$  row and  $i^{\text{th}}$  column.

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Appendix A Derivation of the Inter-Intraparticle Adsorption Model Equations.

DERIVATION AND DE-DIMENSIONALIZING OF THE INTER-INTRA-PARTICLE ADSORPTION MODEL

A. DERIVATION OF THE INTERPARTICLE GAS PHASE MASS BALANCE

CONSIDER AN ELEMENT OF BED  $\Delta x$  IN LENGTH WITH A CROSS SECTIONAL AREA OF  $S$ .

1. THE RATE AT WHICH SOLUTE ENTERS THE ELEMENT AT  $x$  BY HYDRODYNAMIC FLOW IS:\*

$$(e S G_s y / (1-y))_x \quad (i)$$

2. THE RATE AT WHICH SOLUTE LEAVES THE ELEMENT AT  $x + \Delta x$  BY HYDRODYNAMIC FLOW IS:

$$(e S G_s y / (1-y))_{x+\Delta x} \quad (ii)$$

3. THE RATE AT WHICH SOLUTE ENTERS AT  $x$  BY DIFFUSION IS:

$$[-(e S D_E P / RT) dy/dx]_x$$

OR

$$-(e S D_E p_g dy/dx)_x \quad (iii)$$

4. THE RATE AT WHICH SOLUTE LEAVES AT  $x + \Delta x$  BY DIFFUSION IS:

$$-(e S D_E p_g dy/dx)_{x+\Delta x} \quad (iv)$$

5. THE RATE AT WHICH SOLUTE LEAVES ALL THE PARTICLES INTO THE ELEMENT IS:

$$-(4\pi R^2) \rho_g D_A \beta N (dy_i/dr)_{r=R} \Delta x S \quad (v)$$

\* see separate NOMENCLATURE LIST at the end of this appendix for definition of terms.

EQUATIONS (i), (ii), (iii), (iv), AND (v) MAY BE COMBINED ACCORDING TO THE RELATION:

$$\text{INPUT} - \text{OUTPUT} = \text{ACCUMULATION}$$

WHERE THE ACCUMULATION TERM IS GIVEN BY:

$$(\epsilon S \rho_g dy/dt)_{\bar{x}} \Delta x \quad (\text{vi})$$

WHERE  $(x < \bar{x} < x + \Delta x)$ ,

OR:

$$\begin{aligned} & [(\epsilon S G_s y/(1-y))_x - (\epsilon S G_s y/(1-y))_{x+\Delta x}] \\ & + [(-\epsilon S D_E \rho_g dy/dx)_x - (-\epsilon S D_E \rho_g dy/dx)_{x+\Delta x}] \\ & + [- (4\pi R^2) \rho_g D_A \beta N (dy_i/dr)_{r=R} S \Delta x] \\ & = (\epsilon S \rho_g dy/dt) \Delta x \quad (\text{vii}) \end{aligned}$$

DIVIDING EQUATION (vii) BY  $\epsilon S \Delta x$  YIELDS:

$$\begin{aligned} & - [ (G_s y/(1-y))_{x+\Delta x} - (G_s y/(1-y))_x ] / \Delta x \\ & + [ (D_E \rho_g dy/dx)_{x+\Delta x} - (D_E \rho_g dy/dx)_x ] / \Delta x \\ & - (4\pi R^2) \rho_g D_A (\beta/\epsilon) N (dy_i/dr)_{r=R} = \rho_g dy/dt \quad (\text{viii}) \end{aligned}$$

TAKING THE LIMIT OF EQUATION (viii) AS  $\Delta x \rightarrow 0$ , YIELDS THE FOLLOWING:

$$\begin{aligned} D_E \rho_g d^2y/dx^2 - (G_s/(1-y)^2) dy/dx - 4\pi R^2 \rho_g D_A (\beta/\epsilon) N (dy_i/dr)_{r=R} \\ = \rho_g dy/dt \quad (\text{ix}) \end{aligned}$$

OR

$$\begin{aligned} D_E d^2y/dx^2 - [G_s/\rho_g(1-y)] (1/(1-y)) dy/dx - 4\pi R^2 D_A (\beta/\epsilon) N (dy_i/dr)_{r=R} \\ = dy/dt \quad (\text{x}) \end{aligned}$$

NOW

$$G = G_s/(1-y) = \rho_g V$$



OR:

$$v = G_s / \rho_g (1-y) \quad ; \text{ WHICH IS THE LINEAR INTERSTITIAL VELOCITY; } \quad (xi)$$

AND:

WHERE  $N \triangleq$  NUMBER OF SPHERES PER UNIT VOLUME OF BED

$$\frac{4}{3} \pi R^3 N = 1 - \epsilon$$

OR:

$$N = 3(1-\epsilon) / 4\pi R^3 \quad (xii)$$

SUBSTITUTION OF EQUATIONS (xi) AND (xii) INTO EQUATION (x) YIELDS THE FOLLOWING:

$$D_E \frac{d^2 y}{dx^2} - [v/(1-y)] \frac{dy}{dx} - [3(1-\epsilon) \rho_A / \epsilon R] \left( \frac{dy_i}{dr} \right)_{r=R} = \frac{dy}{dt}$$

ASSUMING  $(1-y) \cong 1$ , THE ABOVE MAY BE LINEARIZED TO YIELD:

$$D_E \frac{d^2 y}{dx^2} - v \frac{dy}{dx} - [3(1-\epsilon) \rho_A / \epsilon R] \left( \frac{dy_i}{dr} \right)_{r=R} = \frac{dy}{dt} \quad \dots (xiii)$$

EQUATION (xiii) IS THE DIMENSIONAL FORM OF THE LINEARIZED, INTERPARTICLE GAS PHASE MASS BALANCE.

#### B. DERIVATION OF THE INTRAPARTICLE GAS PHASE MASS BALANCE

CONSIDER A SPHERICAL SHELL OF INSIDE RADIUS  $r$  AND THICKNESS  $\Delta r$ .

1. THE INPUT OF SOLUTE DUE TO DIFFUSION IS:

$$(4\pi r^2 D_A \rho_g \frac{dy_i}{dr})_r \quad (xiv)$$

2. THE OUTFLOW OF SOLUTE DUE TO DIFFUSION IS:

$$(4\pi r^2 D_A \rho_g \frac{dy_i}{dr})_{r+\Delta r} \quad (xv)$$

3. THE ACCUMULATION OR TRANSFER OF MATERIAL TO THE ADSORBED PHASE WITHIN THE INCREMENT  $\Delta r$  IS GIVEN

BY:

$$(4\pi r^2(1-\theta) \rho_L \frac{dc_a}{dt})_F \Delta r \quad (xvi)$$

WHERE:  $r < \bar{r} < r + \Delta r$

4. THE ACCUMULATION TERM FOR THE GAS PHASE WITHIN THE PARTICLE IS GIVEN BY:

$$(4\pi r^2 \beta \rho_g \frac{dy_i}{dt})_F \Delta r \quad (xvii)$$

WHERE:  $r < \bar{r} < r + \Delta r$

USING THE RELATION, INPUT-OUTPUT = ACCUMULATION, EQUATIONS (xiv), (xv), (xvi), AND (xvii) MAY BE COMBINED TO YIELD:

$$\begin{aligned} & \left[ (4\pi r^2 D_A \beta \rho_g \frac{dy_i}{dr})_{r+\Delta r} - (4\pi r^2 D_A \beta \rho_g \frac{dy_i}{dr})_r \right] \\ & - (4\pi r^2(1-\theta) \rho_L \frac{dc_a}{dt})_F \Delta r \\ & = (4\pi r^2 \beta \rho_g \frac{dy_i}{dt})_F \Delta r \quad (xviii) \end{aligned}$$

DIVIDING EQUATION (xviii) THROUGH BY  $(4\pi \beta \rho_g \Delta r)$  AND TAKING THE LIMIT AS  $\Delta r \rightarrow 0$ , LEADS TO THE FOLLOWING REDUCTION OF EQUATION (xviii):

$$D_A \left[ \frac{d^2 y_i}{dr^2} + \left( \frac{2}{r} \right) \frac{dy_i}{dr} \right] - \left[ (1-\theta) \rho_L / \beta \rho_g \right] \frac{dc_a}{dt} = \frac{dy_i}{dt} \quad \dots (xix)$$

EQUATION (xix) IS THE DIMENSIONAL FORM OF THE INTRAPARTICLE GAS PHASE MASS BALANCE.

#### C. DERIVATION OF THE ADSORBED PHASE MASS BALANCE.

ASSUMING NO DIFFUSION OR BULK FLOW OF ADSORBED MATERIAL WITHIN THE ADSORBED PHASE, THE FOLLOWING RELATION MAY BE USED:

$$(1-\theta) \rho_L \frac{dc_a}{dt} = k_{ads} \beta \rho_g (y_i - y_i^*) \quad (xx)$$

D. A THERMODYNAMIC RELATIONSHIP BETWEEN THE INTRAPARTICLE PHASE AND THE ADSORBED PHASE.

IT IS ASSUMED THAT A LINEAR RELATIONSHIP MAY BE USED:

$$y_i^* = m'c_a \quad (xxi)$$

E. AN EXTERNAL (INTER-INTRAPARTICLE) BOUNDARY CONDITION

THE CONDITION AT THE SPHERE SURFACE WHEN THERE IS A RESISTANCE TO MASS TRANSFER CAN BE GIVEN BY:

$$\rho_s \rho_{DA} \partial y_i / \partial r = k_y (y - y_i); \text{ when } r = R \quad \dots (xxii)$$

THIS EQUATION DEFINES THE MASS TRANSFER COEFFICIENT,  $k_y$ . A LARGE VALUE OF  $k_y$  INDICATES LITTLE RESISTANCE TO MASS TRANSFER AT THE INTER-INTRAPARTICLE REGION INTER-FACE. AS  $k_y$  APPROACHES INFINITY, THE RESISTANCE TO MASS TRANSFER AT THE BOUNDARY APPROACHES ZERO. IN THIS LIMIT, EQUATION (xxii) MAY BE REPLACED BY:

$$y_i = y \quad ; \quad \text{when } r = R \quad (xxiii)$$

F. AN INTERNAL (INTRAPARTICLE) BOUNDARY CONDITION

FROM CONSIDERATIONS OF SYMMETRY, THE FOLLOWING CONDITION MAY BE USED:

$$(\partial y_i / \partial r)_{r=0} = 0 \quad ; \quad t > 0 \quad (xxiv)$$

G. APPROPRIATE INTER PARTICLE BOUNDARY CONDITIONS.

$$y(0, t) = A_{du} \quad (xxv)$$

$$\lim_{x \rightarrow \infty} y(x, t) = \text{finite} \quad ; \quad t > 0 \quad (xxvi)$$

#### H. APPROPRIATE INITIAL CONDITIONS

$$y(x, 0) = 0 \quad ; \quad x \geq 0 \quad (xxvii)$$

$$y_i(x, r, 0) = 0 \quad ; \quad x \geq 0, r \geq 0 \quad (xxviii)$$

$$C_a(x, r, 0) = 0 \quad ; \quad x \geq 0, r \geq 0 \quad (xxix)$$

IN ORDER TO MAKE THE PREVIOUSLY DERIVED AND POSTULATED EQUATIONS MORE GENERAL, IT IS NECESSARY AND APPROPRIATE TO DEFINE AND IMPLEMENT DIMENSIONLESS VARIABLES AND COEFFICIENTS.

ONE MAY DEFINE THE FOLLOWING QUANTITIES:

1. A DIMENSIONLESS TIME:

$$\theta = vt/L \quad (xxx)$$

2. A DIMENSIONLESS AXIAL LENGTH:

$$z = x/L \quad (xxxi)$$

3. A DIMENSIONLESS RADIAL LENGTH:

$$r = r/R \quad (xxxii)$$

4. A DIMENSIONLESS AXIAL DIFFUSION NUMBER:

$$Pe_E = VL/D_E \quad (xxxiii)$$

5. A DIMENSIONLESS MASS TRANSFER COEFFICIENT:

$$N_{\text{TOG}} = k_y a_p L / EG \quad (xxxiv)$$

6. A DIMENSIONLESS INTRAPARTICLE DIFFUSION NUMBER:

$$Pe_A = VL/D_A \quad (xxxv)$$

7. THE RATIO OF MOLES OF FLUID PRESENT IN THE PARTICLE TO THE MOLES OF ADSORPTION SITES WITHIN THE PARTICLE:

$$R_I = \rho_g / \rho_L (1-\beta) C_{at} \quad (xxxvi)$$

8. A DIMENSIONLESS RATE OF ADSORPTION COEFFICIENT:

$$N_{Ru} = k_{ads} L / V \quad (xxxvii)$$

9. A DIMENSIONLESS ADSORBED PHASE CONCENTRATION:

$$\chi_a = C_a / C_{at} \quad (xxxviii)$$

THE PRECEDING DEFINITIONS MAY BE APPLIED TO THE DIMENSIONAL SET OF EQUATIONS GIVEN. AFTER THE SUBSEQUENT MANIPULATIONS, A SET OF DIMENSIONLESS EQUATIONS IS REALIZED. THE RESULTS ARE:

THE INTERPARTICLE GAS PHASE MASS BALANCE IS:

$$\frac{1}{Pe_E} \frac{d^2 y}{dz^2} - \frac{dy}{dz} - N_{toG} (y - y_i)_{i=1} = \frac{dy}{d\theta} \quad (xxxix)$$

THE INTRAPARTICLE GAS PHASE MASS BALANCE IS:

$$\frac{1}{Pe_A} \left( \frac{L}{R} \right)^2 \left[ \frac{d^2 y_i}{dr^2} + \frac{2}{r} \frac{dy_i}{dr} \right] - N_{Ru} (y_i - y_i^*) = dy_i / d\theta \quad (xl)$$

THE ADSORBED PHASE MASS BASE:

$$\left( \frac{1}{R_I} \right) d\chi_a / d\theta = N_{Ru} (y_i - y_i^*) \quad (xli)$$

A THERMODYNAMIC RELATIONSHIP BETWEEN THE INTRAPARTICLE AND ADSORBED PHASES:

$$y_i^* = m \chi_a \quad (xlii)$$

AN EXTERNAL (INTER-INTRAPARTICLE) BOUNDARY CONDITION:

$$\left[ \frac{\rho_{ap} L(\frac{L}{R})}{\epsilon \rho_{at}} \right] \frac{dy_i}{dr} = N \log(y - y_i);$$

when  $r = 1 \dots (xliii)$

AN INTERNAL (INTRAPARTICLE) BOUNDARY CONDITION:

$$\frac{dy_i}{dr} = 0 \quad ; \quad r = 0 \quad (xliiv)$$

APPROPRIATE INTER PARTICLE BOUNDARY CONDITIONS:

$$y(0, \theta) = A_{\delta(\theta)} \quad (xlv)$$

$$\lim_{z \rightarrow \infty} y(z, \theta) = \text{finite} \quad ; \quad \theta > 0 \quad (xlvi)$$

APPROPRIATE INITIAL CONDITIONS:

$$y(z, 0) = 0 \quad ; \quad z > 0 \quad (xlvii)$$

$$y_i(z, r, 0) = 0 \quad ; \quad z > 0, r \geq 0 \quad (xlviii)$$

$$x_a(z, r, 0) = 0 \quad ; \quad z > 0, r \geq 0 \quad (xlix)$$

IT SHOULD BE NOTED THAT PRESENTATION OF ABOVE EQUATIONS IN THE MAIN BODY OF THE REPORT MAY OMIT THE SUBSCRIPT  $a$  ON  $x_a$  AND THE PARENTHESISED SUBSCRIPT  $(\theta)$  ON  $A_{\delta(\theta)}$ .

## NOMENCLATURE

- $a_p$  = RATIO OF INTERFACIAL AREA TO PACKED VOLUME,  $(= 3(1-\epsilon)/R)$ .  
 $A_{d(t)}$  = UNIT IMPULSE FOR REAL TIME, DIRAC DELTA FUNCTION.  
 $A_{d(\theta)}$  = UNIT IMPULSE FOR DIMENSIONLESS TIME, DIRAC DELTA FUNCTION.  
 $C_a$  = MOLES OF ADSORBED GAS PER UNIT WEIGHT OF ADSORBENT.  
 $C_{aT}$  = MOLES OF ADSORBED GAS PER UNIT WEIGHT OF ADSORBENT WHEN ALL ADSORPTION SITES ARE OCCUPIED.  
 $D_A$  = INTRAPARTICLE DIFFUSION COEFFICIENT.  
 $D_E$  = INTERPARTICLE AXIAL DIFFUSION COEFFICIENT.  
 $G$  = MOLAR VELOCITY OF GAS STREAM.  
 $G_S$  = MOLAR VELOCITY OF CARRIER GAS.  
 $K_{ads}$  = ADSORPTIVE RATE CONSTANT DEFINED AS THE TIME RATE OF CHANGE OF THE RATIO OF MOLES OF ADSORBED PHASE PER UNIT VOLUME OF PARTICLE TO THE MOLES OF INTRAPARTICLE PHASE PER UNIT VOLUME OF PARTICLE VOID VOLUME.  
 $K_y$  = FILM TRANSFER COEFFICIENT DEFINED AS THE FILM RATE OF TRANSFER OF MOLES PER EXTERNAL SURFACE AREA PER PARTICLE.  
 $L$  = LENGTH OF CHROMATOGRAPH COLUMN.  
 $m$  = EQUILIBRIUM CONSTANT DEFINED IN EQUATION (XIIa).  
 $m'$  = EQUILIBRIUM CONSTANT DEFINED IN EQUATION (XXa).  
 $N$  = NUMBER OF SPHERES PER UNIT VOLUME OF BED.  
 $N_{Ru}$  = DIMENSIONLESS ADSORPTION RATE COEFFICIENT.  
 $N_{To6}$  = DIMENSIONLESS MASS TRANSFER COEFFICIENT.  
 $p$  = PRESSURE IN THE BED.  
 $Pe_A$  = DIMENSIONLESS INTRAPARTICLE DIFFUSION COEFFICIENT.  
 $Pe_E$  = DIMENSIONLESS INTERPARTICLE AXIAL DIFFUSION COEFFICIENT.  
 $r$  = DIMENSIONAL RADIAL DISTANCE WITHIN THE PARTICLE.  
 $\bar{r}$  = DIMENSIONAL POSITION WITHIN THE PARTICLE ELEMENT OF THICKNESS  $\Delta r$ .  
 $\bar{r}_L$  = DIMENSIONLESS INTRAPARTICLE LENGTH.  
 $R$  = PARTICLE RADIUS.  
 $R_g$  = GAS CONSTANT.  
 $R_I$  = RATIO OF MOLES OF FLUID WITHIN THE PARTICLE TO THE MOLES OF ADSORPTION SITES IN THE PARTICLE.  
 $S$  = CROSS-SECTIONAL ELEMENT OF THE BED.  
 $t$  = DIMENSIONAL TIME.  
 $T$  = TEMPERATURE OF THE BED.  
 $V$  = LINEAR INTERSTITIAL VELOCITY.  
 $x$  = DIMENSIONAL AXIAL POSITION IN THE BED.  
 $\bar{x}$  = DIMENSIONAL AXIAL POSITION WITHIN THE ELEMENT  $\Delta x$ .

- $x_a$  = MOLE FRACTION OF FILLED ADSORPTION SITES, DIMENSIONLESS.  
 $y$  = CONCENTRATION IN THE INTERPARTICLE REGION, DIMENSIONLESS.  
 $y_i$  = CONCENTRATION IN THE INTRAPARTICLE REGION, DIMENSIONLESS.  
 $y_i^*$  = EQUILIBRIUM CONCENTRATION IN THE INTRAPARTICLE REGION, DIMENSIONLESS.  
 $z$  = DIMENSIONLESS AXIAL (INTERPARTICLE) LENGTH.

#### GREEK LETTERS

- $\beta$  = PARTICLE POROSITY OF VOID FRACTION.  
 $\Delta x$  = DIMENSIONAL AXIAL INCREMENT WITHIN THE BED.  
 $\Delta r$  = DIMENSIONAL RADIAL INCREMENT WITHIN THE PARTICLE.  
 $\epsilon$  = BED VOID FRACTION.  
 $\rho_g$  = MOLAR DENSITY OF THE GAS.  
 $\rho_L$  = APPARENT DENSITY OF THE PARTICLE, UNIT WEIGHT OF ADSORBENT PER UNIT VOLUME OF PARTICLE.  
 $\theta$  = DIMENSIONLESS TIME.



### DETAILS OF MOMENT ANALYSIS FOR PULSED SYSTEMS\*

THE IMPULSE RESPONSE OF A CHEMICAL REACTOR IS SOMETIMES REFERRED TO AS THE RESIDENCE TIME FREQUENCY DISTRIBUTION. THE STEP RESPONSE, THE INTEGRAL OF THE IMPULSE RESPONSE, IS THEN TERMED THE CUMULATIVE RESIDENCE TIME DISTRIBUTION. THESE QUANTITIES RESEMBLE THE DISTRIBUTIONS STUDIED IN STATISTICAL ANALYSIS; I.E., THE PROBABILITY DISTRIBUTION FUNCTION AND THE CUMULATIVE DISTRIBUTION FUNCTION.

ONE MAY CHARACTERIZE A PARTICULAR DISTRIBUTION FUNCTION,  $f(\theta)$ , BY ITS MOMENTS. THE MOMENTS CAN BE DEFINED BY THE FOLLOWING EQUATION:

$$M_n = \frac{\int_0^{\infty} \theta^n f(\theta) d\theta}{\int_0^{\infty} f(\theta) d\theta} \quad (1)$$

THE MOMENTS DEFINED BY THE ABOVE EQUATION ARE TERMED ABSOLUTE MOMENTS OR MOMENTS ABOUT THE ORIGIN. THE DENOMINATOR IN EQUATION (1) IS JUST THE AREA UNDER THE CURVE,  $f(\theta)$ .

THE RELATIONSHIPS OF THE VARIOUS MOMENTS TO THE LAPLACE TRANSFORM CAN BE DISCERNED WHEN THE TRANSFORM IS WRITTEN IN TERMS OF AN INFINITE SERIES.

$$\text{LET: } \tilde{f}(s) = \mathcal{L}[f(\theta)]$$

THEREFORE:

$$\tilde{f}(s) = \int_0^{\infty} e^{-s\theta} f(\theta) d\theta = \int_0^{\infty} (1 - s\theta + \frac{1}{2}s^2\theta^2 - \frac{1}{6}s^3\theta^3 + \frac{1}{24}s^4\theta^4 - \dots) f(\theta) d\theta$$

CARRYING THE INTEGRAL THROUGH AND FACTORING OUT  $\int_0^{\infty} f(\theta) d\theta$  GIVES:

$$\tilde{f}(s) = \int_0^{\infty} f(\theta) d\theta \left\{ 1 - \frac{s \int_0^{\infty} \theta f(\theta) d\theta}{\int_0^{\infty} f(\theta) d\theta} + \frac{\frac{1}{2}s^2 \int_0^{\infty} \theta^2 f(\theta) d\theta}{\int_0^{\infty} f(\theta) d\theta} - \frac{\frac{1}{6}s^3 \int_0^{\infty} \theta^3 f(\theta) d\theta}{\int_0^{\infty} f(\theta) d\theta} + \frac{\frac{1}{24}s^4 \int_0^{\infty} \theta^4 f(\theta) d\theta}{\int_0^{\infty} f(\theta) d\theta} - \dots \right\}$$

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\* SOME ASPECTS OF THIS DEVELOPMENT PARALLEL THOSE PRESENTED BY DOUGLAS, J.M., "Process Dynamics and Control, Volume 1: Analysis of Dynamic Systems," Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1972, pp. 256-259; 265-268.

RECALLING THE DEFINITION OF THE  $M_n^{\text{th}}$  MOMENT GIVEN IN EQUATION (2), THE TRANSFORM CAN NOW BE WRITTEN IN TERMS OF THE MOMENTS:

$$\tilde{f}(s) = \left( \int_0^{\infty} f(\theta) d\theta \right) \left[ 1 - sM_1 + \frac{1}{2}s^2M_2 - \frac{1}{6}s^3M_3 + \frac{1}{24}s^4M_4 - \dots \right]$$

NOW, ONE CAN SHOW THE RELATIONSHIP OF THE LAPLACE TRANSFORM TO THE MOMENT FUNCTION:

$$\lim_{s \rightarrow 0} \int_0^{\infty} e^{-s\theta} f(\theta) d\theta = \int_0^{\infty} f(\theta) d\theta = A_f$$

WHERE:  $A_f \triangleq$  THE AREA UNDER THE CURVE  $f(\theta)$ .

AND:

$$\begin{aligned} \lim_{s \rightarrow 0} \frac{d}{ds} \left[ \int_0^{\infty} e^{-s\theta} f(\theta) d\theta \right] &= \lim_{s \rightarrow 0} \int_0^{\infty} -\theta e^{-s\theta} f(\theta) d\theta \\ &= - \left( \int_0^{\infty} f(\theta) d\theta \right) \left( \frac{\int_0^{\infty} \theta f(\theta) d\theta}{\int_0^{\infty} f(\theta) d\theta} \right) \end{aligned}$$

$$\therefore \lim_{s \rightarrow 0} \frac{d}{ds} [\tilde{f}(s)] = -A_f M_1$$

ALSO:

$$\begin{aligned} \lim_{s \rightarrow 0} \frac{d^2}{ds^2} \left[ \int_0^{\infty} e^{-s\theta} f(\theta) d\theta \right] &= \lim_{s \rightarrow 0} \int_0^{\infty} \theta^2 e^{-s\theta} f(\theta) d\theta \\ &= \int_0^{\infty} \theta^2 f(\theta) d\theta \end{aligned}$$

$$\lim_{s \rightarrow 0} \frac{d^2}{ds^2} [\tilde{f}(s)] = A_f M_2$$

THESE EXPRESSIONS LEAD TO THE MORE GENERAL RELATIONSHIP:

$$\lim_{s \rightarrow 0} \frac{d^n}{ds^n} \left[ \int_0^{\infty} e^{-s\theta} f(\theta) d\theta \right] = (-1)^n \int_0^{\infty} \theta^n f(\theta) d\theta$$

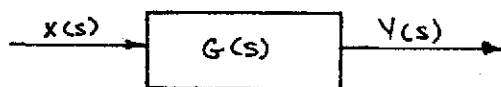
OR:

$$\lim_{s \rightarrow 0} \frac{d^n}{ds^n} [\tilde{f}(s)] = (-1)^n A_f M_n$$

SOLVING FOR  $M_n$  AND INSERTING THE DEFINITION OF  $A_f$  YIELDS THE RELATIONSHIP FOR THE MOMENTS TO THE LAPLACE TRANSFORM:

$$M_n = (-1)^n \lim_{s \rightarrow 0} \frac{d^n}{ds^n} [\tilde{f}(s)] / \lim_{s \rightarrow 0} \tilde{f}(s) \quad (ii)$$

THE PRECEDING CAN BE USED TO OBTAIN INFORMATION FOR SYSTEMS FORCED BY ARBITRARY PULSE INPUTS. CONSIDER THE FOLLOWING TRANSFER FUNCTION BLOCK DIAGRAM:



WHERE:

$X(s) = \mathcal{L}[x(\theta)]$ ;  $x(\theta)$  IS THE FORCING FUNCTION.

$Y(s) = \mathcal{L}[y(\theta)]$ ;  $y(\theta)$  IS THE OUTPUT WAVE.

$G(s)$  = SYSTEM TRANSFER FUNCTION, WHICH IS THE LAPLACE TRANSFORM OF THE IMPULSE RESPONSE OF THE SYSTEM.

THE BLOCK DIAGRAM YIELDS THE FOLLOWING RELATIONSHIP:

$$Y(s) = G(s) X(s) \quad (iii)$$

NOW EACH TRANSFORM CAN BE CONSIDERED IN TERMS OF ITS RESPECTIVE MOMENTS:

$$X(s) = A_x \left[ 1 - sM_{1x} + \frac{1}{2}s^2M_{2x} - \frac{1}{6}s^3M_{3x} + \frac{1}{24}s^4M_{4x} - \dots \right] \quad (iv)$$

$$Y(s) = A_y \left[ 1 - sM_{1y} + \frac{1}{2}s^2M_{2y} - \frac{1}{6}s^3M_{3y} + \frac{1}{24}s^4M_{4y} - \dots \right] \quad (v)$$

$$G(s) = A_g \left[ 1 - sM_{1g} + \frac{1}{2}s^2M_{2g} - \frac{1}{6}s^3M_{3g} + \frac{1}{24}s^4M_{4g} - \dots \right] \quad (vi)$$

SUBSTITUTING EQUATIONS (iv), (v) AND (vi) INTO EQUATION (iii) YIELDS THE FOLLOWING:

$$\begin{aligned}
& A_y \left[ 1 - s M_{1y} + \frac{1}{2} s^2 M_{2y} - \frac{1}{6} s^3 M_{3y} + \frac{1}{24} s^4 M_{4y} - \dots \right] \\
&= A_x A_G \left[ 1 - s (M_{1x} + M_{1G}) + \frac{1}{2} s^2 (M_{2x} + 2M_{1x} M_{1G} + M_{2G}) \right. \\
&\quad \left. - \frac{1}{6} s^3 (M_{3x} + 3M_{1G} M_{2x} + 3M_{2G} M_{1x} + M_{3G}) \right. \\
&\quad \left. + \frac{1}{24} s^4 (M_{4x} + 4M_{1G} M_{3x} + 6M_{2G} M_{2x} + 4M_{3G} M_{1x} + M_{4G}) \right. \\
&\quad \left. - \dots \right] \quad \dots \text{(vii)}
\end{aligned}$$

EQUATING THE COEFFICIENTS OF THE POWERS OF  $s$  IN EQUATION (vii) YIELDS THE FOLLOWING RELATIONSHIPS:

$$A_y = A_x A_G \quad \text{(viii)}$$

$$M_{1y} = M_{1x} + M_{1G} \quad \text{(ix)}$$

$$M_{2y} = M_{2x} + 2M_{1x} M_{1G} + M_{2G} \quad \text{(x)}$$

$$M_{3y} = M_{3x} + 3M_{1G} M_{2x} + 3M_{2G} M_{1x} + M_{3G} \quad \text{(xi)}$$

EQUATION (viii) STATES THAT THE PRODUCT OF THE AREA UNDER THE IMPULSE RESPONSE AND THE AREA UNDER THE INPUT PULSE EQUALS THE AREA UNDER THE OUTPUT PULSE.

EQUATION (ix) STATES THAT THE MEAN OF THE OUTPUT OCCURS AT THE SUM OF THE MEANS OF THE INPUT AND IMPULSE.

THIS DISCUSSION COULD BE CONTINUED IN TERMS OF THE HIGHER ABSOLUTE MOMENTS BUT FOR  $n \geq 2$ , INTEREST CENTERS ON MOMENTS ABOUT THE MEAN,  $M_1$ . THESE MOMENTS ARE DEFINED BY THE FOLLOWING:

$$\bar{M}_n = \int_0^{\infty} (\theta - M_1)^n f(\theta) d\theta / \int_0^{\infty} f(\theta) d\theta \quad ; \quad n \geq 2 \quad \text{(xii)}$$

EXPANSION OF THE ABOVE YIELDS EXPRESSIONS FOR  $\bar{M}_n$  IN TERMS OF THE MOMENTS  $M_n$ .

FOR  $n=2$ , THE RESULT IS:

$$\bar{M}_2 = M_2 - M_1^2 \quad \text{(xiii)}$$

$\bar{M}_2$  IS THE VARIANCE OF THE DISTRIBUTION FUNCTION.

FOR  $n=3$ , THE RESULT IS:

$$\bar{M}_3 = M_3 - 3M_1M_2 + 2M_1^3$$

USING EQUATION (XIII) THIS REDUCES TO:

$$\bar{M}_3 = M_3 - 3M_1\bar{M}_2 - M_1^3 \quad (XIV)$$

USING EQUATIONS (XII) AND (XIV), ONE CAN REWRITE EQUATIONS (X) AND (XII) IN TERMS OF THE RESPECTIVE MOMENTS ABOUT THE MEAN,  $\bar{M}_{3Y}$ ,  $\bar{M}_{3X}$ ,  $\bar{M}_{3G}$ ,  $\bar{M}_{2Y}$ ,  $\bar{M}_{2X}$ ,  $\bar{M}_{2G}$ . THEN USING EQUATION (IX), THE RESULTS ARE:

$$\bar{M}_{2Y} = \bar{M}_{2X} + \bar{M}_{2G} \quad (XV)$$

AND

$$\bar{M}_{3Y} = \bar{M}_{3X} + \bar{M}_{3G} \quad (XVI)$$

THUS THE VARIANCE OF THE OUTPUT IS THE SUM OF THE VARIANCE OF THE INPUT AND THE IMPULSE RESPONSE. THE THIRD MOMENT ABOUT THE ORIGIN OF THE RESPONSE (RELATED TO SKEW) IS THE SUM OF THE THIRD MOMENTS ABOUT THE RESPECTIVE MEANS OF THE INPUT AND IMPULSE RESPONSE.

Appendix C Derivation of the Transfer Function for the Inter-Intraparticle Adsorption Model.

DERIVATION OF THE TRANSFER FUNCTION FOR THE INTER-INTRA-PARTICLE ADSORPTION MODEL

THE MODEL EQUATIONS ARE:

$$\frac{1}{P_E} \frac{\partial^2 y}{\partial z^2} - \frac{\partial y}{\partial z} - N_{toG} (y - y_i)_{n=1} = \frac{\partial y}{\partial \theta} \quad (i)$$

$$\left(\frac{L}{R}\right)^2 / P_{EA} \left[ \frac{\partial^2 y_i}{\partial n^2} + \frac{2}{n} \frac{\partial y_i}{\partial n} \right] - N_{Ru} (y_i - y_i^*) = \frac{\partial y_i}{\partial \theta} \quad (ii)$$

$$\frac{1}{R_I} \frac{\partial x_a}{\partial \theta} = N_{Ru} (y_i - y_i^*) \quad (iii)$$

$$y_i^* = m x_a \quad (iv)$$

$$\left[ \left(\frac{P}{E}\right) a_p + \left(\frac{L}{R}\right) / P_{EA} \right] \frac{\partial y_i}{\partial n} = N_{toG} (y - y_i); \text{ when } n=1 \quad (v)$$

$$\frac{\partial y_i}{\partial n} = 0 \quad ; \quad n=0 \quad (vi)$$

$$y(z, 0) = 0 \quad ; \quad z > 0 \quad (vii)$$

$$y_i(z, n, 0) = 0 \quad ; \quad z > 0, n > 0 \quad (viii)$$

$$x_a(z, n, 0) = 0 \quad ; \quad z > 0, n > 0 \quad (ix)$$

$$y(0, \theta) = A \delta = A \cdot \delta(\theta) \quad (x)$$

$$\lim_{z \rightarrow \infty} y(z, \theta) = \text{finite} \quad (xi)$$

ONE MAY NOW PROCEED WITH THE TRANSFER FUNCTION DERIVATION:

FIRST, TAKE THE LAPLACE TRANSFORM OF EQUATION (i);  
THIS YIELDS:

$$\frac{1}{Pe_E} \frac{d^2 y(z,s)}{dz^2} - \frac{dy(z,s)}{dz} - N_{t06} [y(z,s) - y_a(z,r,s)]_{r=1} = s y(z,s) - y(z,0)$$

USING EQUATION (viii), THIS BECOMES:

$$\frac{1}{Pe_E} \frac{d^2 y(z,s)}{dz^2} - \frac{dy(z,s)}{dz} - N_{t06} [y(z,s) - y_a(z,r,s)]_{r=1} = s y(z,s) \quad (xii)$$

NOW, TAKE THE LAPLACE TRANSFORM OF EQUATION (ii):

$$\frac{1}{Pe_A} \left(\frac{L}{R}\right)^2 \left[ \frac{d^2 y_a(z,r,s)}{dr^2} + \frac{2}{r} \frac{dy_a(z,r,s)}{dr} \right] - N_{Ru} [y_a(z,r,s) - y_a^*(z,r,s)] = s y_a(z,r,s) - y_a(z,r,0)$$

USING EQUATION (viii), THIS BECOMES:

$$\frac{1}{Pe_A} \left(\frac{L}{R}\right)^2 \left[ \frac{d^2 y_a(z,r,s)}{dr^2} + \frac{2}{r} \frac{dy_a(z,r,s)}{dr} \right] - N_{Ru} [y_a(z,r,s) - y_a^*(z,r,s)] = s y_a(z,r,s) \quad (xiii)$$

TRANSFORMING EQUATION (iii) YIELDS:

$$\frac{1}{R_I} [s x_a(z,r,s) - x_a(z,r,0)] = N_{Ru} [y_a(z,r,s) - y_a^*(z,r,s)]$$

USING EQUATION (ix), THIS BECOMES:

$$\frac{1}{R_I} s x_a(z,r,s) = N_{Ru} [y_a(z,r,s) - y_a^*(z,r,s)] \quad (xiv)$$

TRANSFORMING EQUATION (iv) YIELDS:

$$y_a^*(z,r,s) = m x_a(z,r,s) \quad (xv)$$

USING EQUATION (xv) IN EQUATION (xiv) GIVES:

$$\frac{1}{m R_I} s y_a^*(z,r,s) = N_{Ru} [y_a(z,r,s) - y_a^*(z,r,s)]$$

SOLVING FOR  $y_a^*(z,r,s)$  GIVES:

$$y_a^*(z,r,s) = \left[ N_{Ru} / ((s/m R_I) + N_{Ru}) \right] y_a(z,r,s) \quad (xvi)$$

NOW EQUATION (XVI) MAY BE SUBSTITUTED INTO EQUATION (XIII) TO ELIMINATE  $y_1^*(z, r, s)$ . AFTER SOME REARRANGEMENT, THE SUBSTITUTION RESULTS IN THE FOLLOWING EQUATION:

$$\frac{d^2 y_1(z, r, s)}{dr^2} + \frac{2}{r} \frac{dy_1(z, r, s)}{dr} - a_1 y_1(z, r, s) = 0 \quad (\text{XVII})$$

WHERE:

$a_1$  = function of  $s$

$$a_1 = \left\{ \left[ \frac{-N_{Ru}}{\left( \frac{s}{mR_T} + N_{Ru} \right)} + N_{Ru} + s \right] \left( \frac{r}{L} \right)^2 P_{eA} \right\} \quad (\text{XVIII})$$

NOW EQUATION (XVII) MUST BE SOLVED FOR  $y_1(z, r, s)$ . REWRITE EQUATION (XVII) AS:

$$r \frac{d^2 y_1(z, r, s)}{dr^2} + 2 \frac{dy_1(z, r, s)}{dr} - a_1 r y_1(z, r, s) = 0 \quad (\text{XIX})$$

PROPOSE A SOLUTION OF THE FORM:

$$y_1(z, r, s) = \frac{C_1}{r} \cosh(\sqrt{a_1} r) + \frac{C_2}{r} \sinh(\sqrt{a_1} r)$$

THE CONSTANTS (WITH RESPECT TO  $r$ ) MUST BE DETERMINED.

APPLICATION OF THE TRANSFORMED BOUNDARY CONDITION, EQUATION (VI) GIVES:

$$C_1 = 0$$

APPLICATION OF THE BOUNDARY CONDITION, EQUATION (V), GIVES (AFTER SOME MANIPULATION):

$$C_2 = b y(z, s) / [(b-1) \sinh(\sqrt{a_1}) + \sqrt{a_1} \cosh(\sqrt{a_1})]$$

WHERE:

$$b = N_{toG} / [(\phi I_E) (L/r) a_p L / P_{eA}] \quad (\text{XX})$$

THEREFORE:

$$y_1(z, r, s) = y(z, s) \left\{ \frac{b}{[(b-1) \sinh(\sqrt{a_1}) + \sqrt{a_1} \cosh(\sqrt{a_1})]} \right\} \frac{\sinh(\sqrt{a_1} r)}{r} \quad (\text{XXI})$$

EQUATION (XXI) IS THE NECESSARY COUPLING RELATIONSHIP NEEDED FOR SOLUTION OF EQUATION (XII). RECALL EQUATION (XII):

$$\frac{1}{P_{eE}} \frac{d^2 y(z, s)}{dz^2} - \frac{dy(z, s)}{dz} - N_{toG} [y(z, s) - y_1(z, r, s)]_{r=1} = s y(z, s) \quad (\text{XII})$$



EVALUATING EQUATION (XXI) AT  $R=1$  YIELDS:

$$y_\lambda(z, 1, s) = y(z, s) \left\{ \frac{b \sinh(\sqrt{a})}{[(b-1) \sinh(\sqrt{a}) + \sqrt{a} \cosh(\sqrt{a})]} \right\}$$

NOW,

LET

$$\lambda(s) = \left\{ \frac{b \sinh(\sqrt{a})}{[(b-1) \sinh(\sqrt{a}) + \sqrt{a} \cosh(\sqrt{a})]} \right\} \quad (XXII)$$

THEREFORE:

$$y_\lambda(z, 1, s) = y(z, s) \lambda(s)$$

SUBSTITUTION OF THIS INTO EQUATION (XXI) AND REARRANGEMENT GIVES:

$$\frac{1}{P_E} \frac{d^2 y(z, s)}{dz^2} - \frac{dy(z, s)}{dz} - \gamma(s) y(z, s) = 0 \quad (XXIII)$$

WHERE:

$$\gamma(s) = \{N \log [1 - \lambda(s)] + s\} \quad (XXIV)$$

IN THE VARIABLE  $z$ , EQUATION (XXIII) IS A LINEAR, HOMOGENEOUS, SECOND-ORDER, CONSTANT COEFFICIENT, ORDINARY DIFFERENTIAL EQUATION. THE CHARACTERISTIC EQUATION OF EQUATION (XXIII) IS:

$$\left(\frac{1}{P_E}\right) P^2 - P - \gamma(s) = 0$$

THE ROOTS ARE:

$$P_{1,2} = \frac{1 \pm \sqrt{1 + 4\gamma(s)/P_E}}{(2/P_E)}$$

THE SOLUTION TO EQUATION (XXIII) IS OF THE FORM:

$$y(z, s) = C_1 \exp[P_1 z] + C_2 \exp[P_2 z] \quad (XXV)$$

WHERE

$$P_1 = P_E (1 + \sqrt{1 + (4\gamma(s)/P_E)}) / 2$$

$$P_2 = P_E (1 - \sqrt{1 + (4\gamma(s)/P_E)}) / 2$$

NOW IT IS NECESSARY TO DETERMINE THE COEFFICIENTS,  $C_1$  AND  $C_2$ .

EQUATION (X) TRANSFORMS TO:

$$y(0, s) = 1 \quad ; \quad (\text{TAKING } A=1) \quad (XXV\dot{A})$$

EQUATION (X\dot{A}) TRANSFORMS TO:

$$\lim_{z \rightarrow \infty} y(z, s) = \text{finite} \quad (XXV\ddot{A})$$

APPLYING EQUATION (XV\dot{A}) TO EQUATION (XV) YIELDS:

$$C_1 = 0$$

APPLYING EQUATION (XV\ddot{A}) TO THE REDUCED EQUATION (XV) YIELDS

$$C_2 = 1$$

THUS THE TRANSFORM FOR THE UNIT IMPULSE RESPONSE OR TRANSFER FUNCTION FOR THE INTERPARTICLE BEHAVIOR HAS BEEN FOUND; I.E.,

$$y(z, s) = \exp[P_2 z]$$

IT IS SUITABLE TO WORK WITH THE TRANSFER FUNCTION FOR THE CHROMATOGRAPH OUTLET AT  $z=1$ . UTILIZATION OF THIS YIELDS (IN SUMMARY):

$$y(1, s) = \exp[P_2 z]$$

WHERE:

$$P_2 = (P_E/2) - \sqrt{(P_E^2/4) + \gamma(s) P_E}$$

$$\gamma(s) = [N_{\text{tog}} (1 - \lambda(s)) + s]$$

$$\lambda(s) = b \sinh(\sqrt{a_1}) / [(b-1) \sinh(\sqrt{a_1}) + \sqrt{a_1} \cosh(\sqrt{a_1})]$$

$$b = N_{\text{tog}} / [(P/E)(L/R) \alpha_P L / P_A]$$

$$a_1(s) = \left\{ \left[ \frac{-N_{\text{eu}}^2}{\left( \frac{3}{mR_L} + N_{\text{eu}} \right)} + N_{\text{ru}} + s \right] \left( \frac{R}{L} \right)^2 P_A \right\}$$

Appendix D Derivation of the Moments of the Impulse Response of the Inter-Intraparticle Adsorption Model.

DERIVATION OF THE MOMENTS OF THE IMPULSE RESPONSE OF THE INTER-INTRAPARTICLE ADSORPTION MODEL

THE LAPLACE TRANSFORM SOLUTION FOR THE IMPULSE RESPONSE OR TRANSFER FUNCTION OF THE MODEL IS:

$$y(1, s) = \exp(P_2) \quad (i')$$

WHERE:

$$P_2 = (P_{E}/2) - \sqrt{(P_{E}^2/4) + \gamma(s)P_{E}} \quad (ii)$$

$$\gamma(s) = [N_{\text{tog}}(1 - \lambda(s)) + s] \quad (iii)$$

$$\lambda(s) = b \sinh(\sqrt{a_1}) / [(b-1)\sinh(\sqrt{a_1}) + \sqrt{a_1} \cosh(\sqrt{a_1})] \quad (iv)$$

$$b = N_{\text{tog}} / [(P/E)(L/R) a_f / P_{EA}] \quad (v)$$

$$q_1(s) = \left\{ \frac{-N_{EII} m_{PI}}{(s + N_{EII} m_{PI})} + N_{EII} + s \right\} \left( \frac{R}{L} \right)^2 P_{EA} \quad (vi)$$

A. CALCULATION OF THE MEAN,  $M_1$ .

$$M_1 = - \lim_{s \rightarrow 0} \frac{d[y(1, s)]}{ds} / \lim_{s \rightarrow 0} [y(1, s)] \quad (vii)$$

NOW

$$\lim_{s \rightarrow 0} [y(1, s)] = 1 \quad (viii)$$

NOW IT IS NECESSARY TO DETERMINE THE NUMERATOR OF EQUATION (vii). USING EQUATION (i):

$$\frac{d[y(1, s)]}{ds} = \exp(P_2) \cdot \frac{d(P_2)}{ds} \quad (ix)$$

NOW FIND THE LIMIT OF ALL  $s$ -DEPENDENT FUNCTIONS DEFINED AS PART OF  $y(1, s)$ :

BY INSPECTION:

$$\lim_{s \rightarrow 0} q_1(s) = 0 \quad (\alpha)$$

USING L'HOPITAL'S RULE:

$$\lim_{s \rightarrow 0} \lambda(s) = 1 \quad (xi)$$

BY INSPECTION

$$\lim_{s \rightarrow 0} \gamma(s) = 0 \quad (xii)$$

AND

$$\lim_{s \rightarrow 0} p_2 = 0 \quad (xiii)$$

BY USING THE RELATION THAT THE LIMIT OF A PRODUCT IS THE PRODUCT OF THE LIMITS, EQUATION (vii) CAN BE REDUCED TO:

$$N_1 = - \left\{ \lim_{s \rightarrow 0} [\exp(p_2)] \cdot \lim_{s \rightarrow 0} \left[ \frac{d(p_2)}{ds} \right] \right\}$$

USING EQUATION (xiii) GIVES

$$N_1 = - \lim_{s \rightarrow 0} \frac{d(p_2)}{ds} \quad (xiv)$$

NOW

$$\lim_{s \rightarrow 0} \frac{d(p_2)}{ds} = \frac{-P_{e2}}{2\sqrt{\frac{P_{e2}^2}{4} + P_{e2} \cdot \lim_{s \rightarrow 0} \gamma(s)}} \cdot \lim_{s \rightarrow 0} \frac{d\gamma(s)}{ds} \quad (xv)$$

AND

$$\lim_{s \rightarrow 0} \frac{d\gamma(s)}{ds} = -N_{\log} \lim_{s \rightarrow 0} \frac{d\lambda(s)}{ds} + 1 \quad (xvi)$$

CHAIN RULE DIFFERENTIATION OF EQUATION (iv) GIVES A COMPLICATED EXPRESSION. THE LIMITS OF THE COMBINATIONS OF HYPERBOLIC FUNCTIONS ARE FOUND BY EXPANDING THE HYPERBOLIC FUNCTIONS IN POWER SERIES AND THEN TAKING THE LIMIT. AFTER SOME MANIPULATION. THE RESULT IS:

$$\lim_{s \rightarrow 0} \frac{d[\lambda(s)]}{ds} = -\frac{1}{3b} \left(1 + \frac{1}{MR_I}\right) \left(\frac{R}{L}\right)^2 P_{eA} \quad (\text{XVII})$$

BACK SUBSTITUTION OF THIS INTO THE PRECEDING EQUATIONS YIELDS (AFTER SOME MANIPULATION):

$$M_1 = 1 + \frac{(1-\epsilon)\beta}{\epsilon} \left(1 + \frac{1}{MR_I}\right)$$

RECOGNIZING THAT

$$\frac{(1-\epsilon)\beta}{\epsilon} \frac{1}{R_I} = \frac{1}{R_0} \quad ; \quad \text{GIVES THE FINAL RESULT:}$$

$$M_1 = 1 + (1-\epsilon)\beta/\epsilon + 1/MR_0 \quad (\text{XVIII})$$

#### B. CALCULATION OF THE SECOND MOMENT ABOUT THE MEAN, $\bar{M}_2$ .

USING EQUATION (VIII), THE EXPRESSION FOR  $\bar{M}_2$  IS:

$$\bar{M}_2 = \lim_{s \rightarrow 0} \frac{d^2}{ds^2} [y(s)] - M_1^2$$

DIFFERENTIATION YIELDS:

$$\bar{M}_2 = \lim_{s \rightarrow 0} \frac{d^2 P_2}{ds^2}$$

PERFORMING THE INDICATED DIFFERENTIATION AND USING THE LIMITS WHICH ALREADY BEEN FOUND GIVES:

$$\bar{M}_2 = \frac{2M_1^2}{P_{eE}} - \lim_{s \rightarrow 0} \frac{d^2 y(s)}{ds^2}$$

PERFORMING THE INDICATED DIFFERENTIATION GIVES:

$$\bar{M}_2 = \frac{2M_1^2}{P_{eE}} + N_{tOG} \lim_{s \rightarrow 0} \frac{d^2 \lambda(s)}{ds^2}$$

PERFORMING THE DIFFERENTIATION AND TAKING THE LIMITS OF THE RESULT INVOLVING HYPERBOLIC FUNCTIONS (USING POWER SERIES EXPANSIONS) GIVES:

$$\bar{M}_2 = \frac{2M_1^2}{P_{eE}} + N_{tOG} \left\{ \left( \lim_{s \rightarrow 0} \frac{da_1}{ds} \right)^2 \left( \frac{2}{45} \frac{1}{b} + \frac{2}{9} \frac{1}{b^2} \right) - \frac{1}{3b} \lim_{s \rightarrow 0} \frac{d^2 a_1}{ds^2} \right\} \quad (xix)$$

NOW

$$\frac{da_1}{ds} = \left[ \frac{N_{Ru}^2 m R_I}{(s + N_{Ru} m R_I)^2} + 1 \right] \left( \frac{R}{L} \right)^2 P_{eA} \quad (xx)$$

AND

$$\frac{d^2 a_1}{ds^2} = \left[ \frac{-2 N_{Ru}^2 m R_I}{(s + N_{Ru} m R_I)^3} \right] \left( \frac{R}{L} \right)^2 P_{eA} \quad (xxi)$$

TAKING THE LIMITS OF EQUATIONS (xx) AND (xxi), SUBSTITUTION INTO EQUATION (xix), AND SOME MANIPULATION GIVES THE RESULT:

$$\bar{M}_2 = \frac{2M_1^2}{P_{eE}} + \frac{2\beta(1-\epsilon)}{\epsilon} \left\{ \left( 1 + \frac{1}{m R_I} \right)^2 \left[ \left( \frac{R}{L} \right)^2 \frac{P_{eA}}{15} + \frac{\beta(1-\epsilon)}{\epsilon N_{tOG}} \right] + \frac{1}{N_{Ru} (m R_I)^2} \right\} \quad (xxii)$$

### C. CALCULATION OF THE THIRD MOMENT ABOUT THE MEAN, $\bar{M}_3$ .

USING EQUATION (xxii) THE EXPRESSION FOR  $\bar{M}_3$  IS:

$$\bar{M}_3 = - \lim_{s \rightarrow 0} \frac{d^3}{ds^3} [y(s, s)] - 3M_1 \bar{M}_2 - M_1^3$$

PERFORMING THE DIFFERENTIATION AND SIMPLIFYING SOMEWHAT GIVES:

$$\bar{M}_3 = - \lim_{s \rightarrow 0} \left( \frac{d^3 P_2}{ds^3} \right) \quad (xxiii)$$

FROM THIS EXPRESSION, THE PROCEDURE IS STRAIGHTFORWARD BUT TEDIOUS. EQUATION (xxiii) IS FIRST REDUCED TO:

$$\bar{M}_3 = \frac{6M_1 \bar{M}_2}{P_{eE}} + \lim_{s \rightarrow 0} \frac{d^3 \lambda(s)}{ds^3}$$

THEN TO:

$$\bar{M}_3 = -N_{t06} \lim_{s \rightarrow 0} \frac{d^3 \lambda(s)}{ds^3} + \frac{6 \mu_1 \bar{M}_2}{P_{eE}}$$

PERFORMING THE DIFFERENTIATION AND TAKING THE LIMITS OF THE RESULT INVOLVING HYPERBOLIC FUNCTIONS (USING POWER SERIES EXPANSIONS) GIVES:

$$\begin{aligned} \bar{M}_3 = & \frac{6 \mu_1 \bar{M}_2}{P_{eE}} + \frac{N_{t06}}{3b} \lim_{s \rightarrow 0} \frac{d^3 a_1}{ds^3} - \frac{N_{t06}}{b} \lim_{s \rightarrow 0} \frac{da_1}{ds} \cdot \lim_{s \rightarrow 0} \frac{d^2 a_1}{ds^2} \left( \frac{2}{15} + \frac{2}{3} \frac{1}{b} \right) \\ & - \frac{N_{t06}}{b} \left( \lim_{s \rightarrow 0} \frac{da_1}{ds} \right)^3 \left( \frac{46}{315} - \frac{4}{45} \frac{1}{b} - \frac{2}{9} \frac{1}{b^2} \right) \end{aligned} \quad (XXIV)$$

NOW

$$\frac{d^3 q_1}{ds^3} = \left[ \frac{6 N_{RU}^2 m R_I}{(s + N_{RU} N_{R2})^4} \right] \left( \frac{R}{L} \right)^2 P_{eA} \quad (XXV)$$

TAKING THE LIMIT OF EQUATION (XXV), SUBSTITUTING IT INTO EQUATION (XXIV), USING PREVIOUS RESULTS, AND MANIPULATION YIELDS THE RESULT:

$$\begin{aligned} \bar{M}_3 = & \frac{6 \mu_1 \bar{M}_2}{P_{eE}} + \frac{6 \beta (1-\epsilon)}{\epsilon} \left\{ \frac{1}{(N_{RU})^2 (m R_I)^3} + \left( 1 + \frac{1}{m R_I} \right) \left( \frac{1}{N_{RU} (m R_I)^2} \right) \left[ \frac{2}{15} \left( \frac{R}{L} \right)^2 P_{eA} + \frac{2 \beta (1-\epsilon)}{\epsilon N_{t06}} \right] \right. \\ & \left. + \left( 1 + \frac{1}{m R_I} \right)^3 \left[ \left( \frac{\beta (1-\epsilon)}{\epsilon N_{t06}} \right)^2 + \frac{2}{15} \frac{\beta (1-\epsilon)}{\epsilon N_{t06}} \left( \frac{R}{L} \right)^2 P_{eA} - \frac{23}{315} \left( \frac{R}{L} \right)^4 P_{eA}^2 \right] \right\} \end{aligned} \quad (XXVI)$$

Appendix E Case I and Case II Transfer Function Derivations and Moment Derivations.

CASE I AND CASE II TRANSFER FUNCTION DERIVATIONS AND MOMENT DERIVATIONS.

A. CASE I

THE PROBLEM IS:

$$\frac{1}{Pe} \frac{d^2 y}{dz^2} - \frac{dy}{dz} = \frac{dy}{d\theta} \quad (i)$$

$$y(z, 0) = 0 \quad ; \quad z > 0 \quad (ii)$$

$$y(0, \theta) = A_0 \quad ; \quad \theta \geq 0 \quad (iii)$$

$$\lim_{z \rightarrow \infty} y(z, \theta) = \text{finite} \quad (iv)$$

TAKING THE LAPLACE TRANSFORM OF (i) AND USING EQUATION (iii) GIVES:

$$\frac{d^2 y(z, s)}{dz^2} - Pe \frac{dy(z, s)}{dz} - s Pe y(z, s) = 0 \quad (v)$$

EQUATION (v) HAS A SOLUTION OF THE FORM:

$$y(z, s) = C_1 \exp(P_1 z) + C_2 \exp(P_2 z)$$

WHERE:

$$P_1 = (Pe/2) + \sqrt{Pe^2/4 + Pe s}$$

$$P_2 = (Pe/2) - \sqrt{Pe^2/4 + Pe s}$$

APPLICATION OF EQUATION (iv), TRANSFORMED, GIVES:

$$C_1 = 0$$

APPLICATION OF THE TRANSFORMED BOUNDARY CONDITION (iii) GIVES:

$$C_2 = 1 \quad (A = 1)$$

THEREFORE, THE TRANSFER FUNCTION OR THE LAPLACE DOMAIN IMPULSE RESPONSE IS:

$$y_z(z, s) = \exp \left\{ \left[ (Pe/2) - \sqrt{(Pe^2/4) + Pe s} \right] z \right\}$$



FOR  $z=1$ , THE BED OUTLET, THIS REDUCES TO:

$$y_I(1,s) = \exp \left[ (Pe/2) - \sqrt{(Pe^2/4) + Pe s} \right] \quad (VI)$$

THE RELATIONSHIP FOR THE FIRST MOMENT ABOUT THE ORIGIN IS:

$$M_{1I} = - \lim_{s \rightarrow 0} \left[ \frac{d y_I(1,s)}{ds} \right]$$

PERFORMING THE DIFFERENTIATION AND TAKING THE LIMIT YIELDS:

$$M_{1I} = 1 \quad (VII)$$

THE RELATIONSHIP FOR THE SECOND MOMENT ABOUT THE MEAN IS:

$$\bar{M}_{2I} = \lim_{s \rightarrow 0} \left[ \frac{d^2 y_I(1,s)}{ds^2} \right] - (M_{1I})^2$$

PERFORMING THE DIFFERENTIATION, TAKING THE LIMIT, AND PERFORMING THE SUBTRACTION YIELDS:

$$\bar{M}_{2I} = 2/Pe \quad (VIII)$$

## B. CASE II

THE PROBLEM IS:

$$\frac{1}{Pe} \frac{\partial^2 y}{\partial z^2} - \frac{\partial y}{\partial z} = \frac{\partial y}{\partial \theta} \quad (IX)$$

$$y(z,0) = 0; \quad z > 0 \quad (X)$$

$$\partial y(z,0)/\partial z = 0; \quad \theta > 0 \quad (XI)$$

$$y(0,\theta) = A_s; \quad \theta > 0 \quad (XII)$$

TAKING THE LAPLACE TRANSFORM OF (IX) AND APPLYING EQUATION (X) GIVES:

$$\frac{\partial^2 y(z,s)}{\partial z^2} - Pe \frac{\partial y(z,s)}{\partial z} - s Pe y(z,s) = 0 \quad (XIII)$$

THE SOLUTION TO (XIII) IS OF THE FORM:

$$y(z,s) = C_1 \exp(P_1 z) + C_2 \exp(P_2 z)$$

WHERE

$$P_1 = (P_0/2) + \sqrt{(P_0^2/4) + P_0 s}$$

$$P_2 = (P_0/2) - \sqrt{(P_0^2/4) + P_0 s}$$

APPLYING THE TRANSFORM OF EQUATION (XA) GIVES:

$$0 = C_1 \left( \frac{P_0}{2} + \sqrt{\frac{P_0^2}{4} + P_0 s} \right) \exp \left[ \left( \frac{P_0}{2} + \sqrt{\frac{P_0^2}{4} + P_0 s} \right) z_0 \right] \\ + C_2 \left( \frac{P_0}{2} - \sqrt{\frac{P_0^2}{4} + P_0 s} \right) \exp \left[ \left( \frac{P_0}{2} - \sqrt{\frac{P_0^2}{4} + P_0 s} \right) z_0 \right] \quad (XIV)$$

APPLYING THE TRANSFORM OF EQUATION (XIV), (A=1), GIVES:

$$1 = C_1 + C_2 \quad (XV)$$

EQUATIONS (XIV) AND (XV) ARE TWO EQUATIONS IN TWO UNKNOWNES; SOLVING FOR  $C_1$  AND  $C_2$  AND SUBSTITUTING INTO THE EXPRESSION FOR  $y(z,s)$  YIELDS:

$$y_{II}(z,s) = \frac{\exp\left(\frac{P_0}{2} z\right) \left\{ \left( \frac{P_0}{2} + \sqrt{\frac{P_0^2}{4} + P_0 s} \right) \exp \left[ -(z-z_0) \sqrt{\frac{P_0^2}{4} + P_0 s} \right] - \left( \frac{P_0}{2} - \sqrt{\frac{P_0^2}{4} + P_0 s} \right) \exp \left[ (z-z_0) \sqrt{\frac{P_0^2}{4} + P_0 s} \right] \right\}}{\left\{ \left( \frac{P_0}{2} + \sqrt{\frac{P_0^2}{4} + P_0 s} \right) \exp \left[ z_0 \sqrt{\frac{P_0^2}{4} + P_0 s} \right] - \left( \frac{P_0}{2} - \sqrt{\frac{P_0^2}{4} + P_0 s} \right) \exp \left[ -z_0 \sqrt{\frac{P_0^2}{4} + P_0 s} \right] \right\}}$$

FOR  $z=1$ , THIS BECOMES:

$$y_{II}(1,s) = \frac{\exp\left(\frac{P_0}{2}\right) \left\{ \left( \frac{P_0}{2} + \sqrt{\frac{P_0^2}{4} + P_0 s} \right) \exp \left[ -(1-z_0) \sqrt{\frac{P_0^2}{4} + P_0 s} \right] - \left( \frac{P_0}{2} - \sqrt{\frac{P_0^2}{4} + P_0 s} \right) \exp \left[ (1-z_0) \sqrt{\frac{P_0^2}{4} + P_0 s} \right] \right\}}{\left\{ \left( \frac{P_0}{2} + \sqrt{\frac{P_0^2}{4} + P_0 s} \right) \exp \left[ z_0 \sqrt{\frac{P_0^2}{4} + P_0 s} \right] - \left( \frac{P_0}{2} - \sqrt{\frac{P_0^2}{4} + P_0 s} \right) \exp \left[ -z_0 \sqrt{\frac{P_0^2}{4} + P_0 s} \right] \right\}} \quad \dots (XVI)$$

THE RELATIONSHIP FOR THE FIRST MOMENT ABOUT THE ORIGIN IS:

$$M_{I,II} = - \lim_{s \rightarrow 0} \left[ \frac{d y_{II}(1,s)}{ds} \right]$$

PERFORMING THE DIFFERENTIATION AND TAKING THE LIMIT YIELDS:

C-2

$$\mu_{II} = 1 + [\exp(-Pe z_0) - \exp(Pe - Pe z_0)] / Pe \quad (xvii)$$

THE RELATIONSHIP FOR THE SECOND MOMENT ABOUT THE MEAN IS:

$$\bar{\mu}_{2II} = \lim_{s \rightarrow 0} \left[ \frac{d^2 \mu_{II}(1, s)}{ds^2} \right] - (\mu_{II})^2$$

PERFORMING THE DIFFERENTIATION, TAKING THE LIMIT, AND PERFORMING THE SUBTRACTION YIELDS:

$$\begin{aligned} \bar{\mu}_{2II} = 2/Pe &+ \exp(Pe - Pe z_0) [(4/Pe) - (4z_0/Pe) - (2/Pe)^2] \\ &+ [\exp(-2Pe z_0)] / (Pe)^2 - [\exp(2Pe - 2Pe z_0)] / (Pe)^2 \\ &\dots (xviii) \end{aligned}$$

## Appendix F Upper and Lower Bounds for the Condition of a Matrix.

UPPER AND LOWER BOUNDS ON THE CONDITION OF A MATRIX

THE CONDITION OF A MATRIX WITH RESPECT TO INVERSION AND A PARTICULAR NORM IS DEFINED AS:

$$K(\underline{A}) = \|\underline{A}\| \cdot \|\underline{A}^{-1}\|$$

WHERE:

$\underline{A}$  IS THE MATRIX BEING CONSIDERED.

$\|\cdot\|$  IS THE MATRIX NORM BEING USED.

NOW LET:

$$\underline{Y} \approx \underline{A}^{-1} ; \text{ WHERE } \underline{Y} \text{ IS THE COMPUTED INVERSE OF } \underline{A}.$$

DEFINE THE MATRIX RESIDUAL,  $\underline{R}$ :

$$\underline{R} = \underline{A}\underline{Y} - \underline{I} ; \text{ WHERE } \underline{I} \text{ IS THE IDENTITY MATRIX.}$$

THEREFORE:

$$\underline{Y} = \underline{A}^{-1} + \underline{A}^{-1}\underline{R}$$

AND:

$$\|\underline{Y}\| \leq \|\underline{A}^{-1}\| \cdot \|\underline{I} + \underline{R}\| \quad (i)$$

ALSO:

$$\underline{A}^{-1} = \underline{Y} \cdot (\underline{I} + \underline{R})^{-1}$$

THIS IMPLIES

$$\|\underline{A}^{-1}\| \leq \|\underline{Y}\| \cdot \|(\underline{I} + \underline{R})^{-1}\| \quad (ii)$$

MULTPLYING EQUATION (i) AND (ii) BY  $\|\underline{A}\|$  AND COMBINING YIELDS:

$$\frac{\|\underline{A}\| \cdot \|\underline{Y}\|}{\|\underline{I} + \underline{R}\|} \leq \|\underline{A}\| \cdot \|\underline{A}^{-1}\| \leq \|\underline{A}\| \cdot \|\underline{Y}\| \cdot \|(\underline{I} + \underline{R})^{-1}\|$$

OR:

$$\frac{\|\underline{A}\| \cdot \|\underline{Y}\|}{\|\underline{I} + \underline{R}\|} \leq K(\underline{A}) \leq \|\underline{A}\| \cdot \|\underline{Y}\| \cdot \|(\underline{I} + \underline{R})^{-1}\| \quad (iii)$$